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The publications include the *Journal*, containing papers communicated to the Society, the *Abstracts*, covering the current literature in pure Chemistry, the *Indexes*, and the *Annual Reports* on the progress of Chemistry.

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The *Meetings*, including those devoted to special lectures, number about 18 annually. Fellows resident outside London may read before British Local Sections of the Society of Chemical Industry papers intended for subsequent publication in the Journal of the Chemical Society.

The annual subscription is £3. Those desiring to become Fellows of the Society should apply for further information to the Secretaries, Burlington House, London, W. 1.

These Rules have been passed PROVISIONALLY by the Committee on Organic Nomenclature of the International Union of Pure and Applied Chemistry. The purpose of publication in their present form is to invite criticism (see pp. 1, 2, 11, 12 of the Rules). Communications on the subject should be addressed to A. J. GREENAWAY, The Orchard, Chertsey, Surrey.

PROPOSED INTERNATIONAL RULES FOR NUMBERING ORGANIC RING SYSTEMS.

By AUSTIN M. PATTERSON.

Preface.

IN 1921 the author suggested to the Board of Editors of the American Chemical Society that it might be advisable to publish a catalogue of organic ring systems with their systematic numberings. The Board decided that it would be, but felt it extremely desirable to secure beforehand a wide agreement among chemists as to the numberings.

Rules for numbering ring systems were drawn up and submitted later to the Committee on Organic Nomenclature of the International Union of Pure and Applied Chemistry, consisting of A. F. Holleman (Netherlands) (*chairman*), A. J. Greenaway (Great Britain), R. Marquis (France), E. Paternò (Italy), A. Pictet (Switzerland), and A. M. Patterson (United States). They were also shown unofficially to the late Prof. Jacobson and to Dr. Stelzner, of Germany. Several drafts were made and much improvement resulted from the criticisms.

In their present form the Rules have been approved by the International Committee for a provisional period of two years, during which they will be open for the criticism of chemists generally. At the end of that period, if no fundamental objections are found to the Rules, the expectation is that they will be finally adopted for use in the journals of the respective countries, with any further improvements or corrections that may have been suggested.

Considerable time has been given to devising a set of Rules that shall be applicable to all systems of simple or fused rings and yet be as simple and clear as possible and preserve a maximum of the numberings now in use. The present article embodies the best results achieved to date. The ring systems described in Beilstein's "Handbuch," Richter's "Lexikon," Stelzner's "Literatur-Register," and the 18 volumes of *Chemical Abstracts* have been carefully checked and the numberings compared.

If and when the Rules are put into effect in the journals, they should be as free from causes for objection as they can be made.

It is urged that anyone having criticisms to make send them promptly to the author, or to his own representative on the International Committee. The question whether hydrogen atoms should be favoured for low numbers in all classes is an important one, and the recommendations of organic chemists are especially desired on this point (see " Position of Double Bonds," under *Comments*).

Publication of the catalogue of ring systems will be deferred, pending the final adoption of the Rules.

Rules and Notes.

Note 1. The word " system " is used to mean a single ring or a combination of rings united one to another by atoms common to both (" fused " systems). Rings united only by a valency bond as in diphenyl ($C_6H_5 \cdot C_6H_5$), or by an intermediate atom or chain as in diphenylmethane ($C_6H_5 \cdot CH_2 \cdot C_6H_5$), are not considered as parts of the same ring system for the purposes of these Rules.

Note 2. Derivatives. Although the following Rules determine the numbering of parent systems *in all degrees of hydrogenation*, it is not the intention to fix the position of hydrogen atoms in all their derivatives. All that is required of derivatives is *that their numbering conform to that of the lowest stage of hydrogenation of the parent system in Classes A II, B and C II, and to that of the saturated form in A I, C I, C III and D I.* For example, the Rules assign the positions 1–4 to the CH_2 groups in " tetralin," which numbering corresponds to the name 1 : 2 : 3 : 4-tetrahydronaphthalene. But this does not prevent the naming and numbering of a hydroxyl derivative of it as 5 : 6 : 7 : 8-tetrahydro-2-naphthol; the numbering of the latter is based on that of naphthalene, the least saturated form of the parent system. (Decision between two or more alternative numberings of derivatives in such cases is a separate matter lying outside the scope of the Rules.) Conversion of a derivative to the lowest stage of hydrogenation of the parent system may involve (1) replacement of substituting atoms or groups by hydrogen, (2) removal of hydrogen atoms in pairs, (3) removal of O_2, CH_3Cl, etc., from ring atoms if the latter can thereby pass to a well-recognised lower state of valence, (4) introduction of quinonoid structure, or rarely (5) conversion of tervalent into quinquevalent nitrogen. It should *not* involve the introduction of triple bonds, two double bonds attached to the same carbon atom, or new bridging bonds. In some cases there will be two or more isomeric least saturated forms which may equally well be regarded as the parent of the derivative.

Note 3. Lowest Numbers. The expression " lowest numbers," as used in connection with the Rules, signifies the numbers yielding

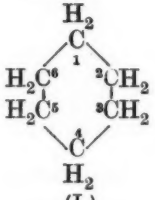
the smallest sum or, if the sums are equally small, those that include the lowest individual number or numbers. Thus, 1,3,5 is lower than 2,4,6; 1,4,5 is lower than 2,3,5; 1,2,5 is lower than 1,3,4; 1,1,3,4 is lower than 1,2,2,4.

A. The system consists of a single ring.

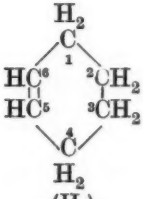
I. The ring is carbocyclic.

Rule 1. Number around the ring in such a manner as to give to hydrogen atoms the lowest numbers possible.

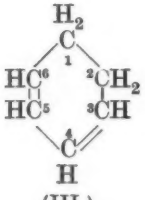
Examples :



(I.)



(II.)



(III.)

(Benzene)
(IV.)

Note 4. Fixed orientations are an aid to memory and should not be neglected. Single rings should be oriented with Position 1 at the top and with the numbers proceeding clockwise around the ring.

II. The ring is heterocyclic.

Rule 2. Choose as starting point a hetero atom of as high a group in the periodic table of the elements, and as low an atomic number in that group, as possible.

Note 5. The following order as determined by the above rule, includes the commonly occurring hetero atoms : O, S, Se, Te, N, P, As, Sb, Si, Sn, Pb, Hg.

Rule 3. With an atom of the preferred kind as 1, *number around the ring in the way that gives to hetero atoms the lowest numbers possible.*

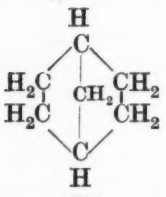
Rule 4. Of two or more numberings conforming to Rules 2 and 3, choose the one that assigns low numbers most nearly in the order of precedence established in Rule 2.

Rule 5. Of two or more numberings conforming to Rules 2–4, choose the one that gives to hydrogen atoms the lowest numbers possible.

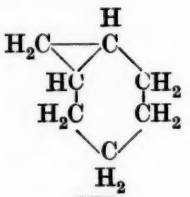
B. The system contains at least two rings of five or more members, but no atomic bridges, crossed valence bridges or free spiro unions.

Note 6. An " atomic bridge " is one that contains atoms (*e.g.*, the bridge in norcamphane, V) as contrasted with a " valency

bridge " (*e.g.*, that in naphthalene, VI, or in norcarane, VII). The " peri " forms frequently encountered among aromatic compounds are included in Class B and are *not* treated as having an atomic bridge, although strictly speaking they do contain one. For example, acenaphthene, VIII, is a " peri " form. Such forms may be regarded as resulting from three ordinary or " ortho " fusions : A with B, B with C, and A with C.


(V.)

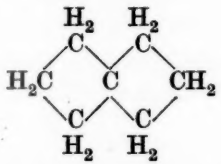
(VI.)


(VII.)

(VIII.)

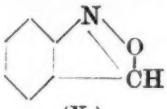
Note 7. " Crossed valency bridges " are valency bridges that are represented by the plane formula as crossing each other, as shown in Example XLVIII.

Note 8. A " spiro union " is one formed by a single atom which is the only common member of two rings. A " free spiro union " is one constituting the *only* union, direct or indirect, between two rings, as in IX. Systems in which the rings are united in some other way (that is, by intermediate rings) as well as by the spiro union are not necessarily excluded from Class B.

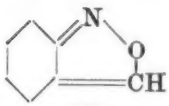
(IX.) 

Note 9. In determining whether or not a system contains at least two rings of five or more members, one counts as component rings *only the smallest number of smallest rings that together will account for all the atoms and valencies.* Thus, in Example VII it is possible to see a 3-ring, a 6-ring and a 7-ring, yet it is called a " 3,6 " system because the 3-ring and the 6-ring together account for all the atoms and valencies and the 7-ring is merely the circumference of the fused 3- and 6-rings; the system does not belong in Class B. Valency bridges which are sometimes used to account for the chemical peculiarities of a compound but which are not absolutely indispensable in representing the formula are not considered in these Rules. The bridge sometimes shown between N and CH in one formula for anthranil (X) is a case in point, for a formula may be

written for it without this bridge, as in XI : it is therefore classed as a 5,6 system and placed in Class B. The middle bridge sometimes shown in the formula for anthracene is another example. Anthracene is treated not as a 4-ring system (XII) but as a 3-ring system (XIII).



(X.)



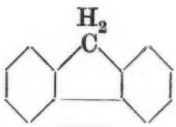
(XI.)

(XII.)

Rule 6. Orient the formula so that the greatest possible number of rings will be in a horizontal row.

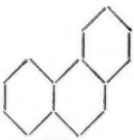
Note 10. Triangles in such a row should have one side vertical, other rings two sides vertical (this requires a deformation of the polygons with an odd number of sides, thus: or). Accordingly, hexagons should have angles, not sides, at top and bottom. Anthracene (XIII) constitutes a horizontal row of three, so do fluorene (XIV) and *s*-indacene (XV); but phenanthrene (XVI) does not.

(XIII.)



(XIV.)

(XV.)

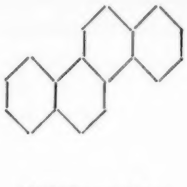

(XVI.)

Rule 7. Of orientations conforming to Rule 6, choose the one that places as many as possible of the remaining rings above and to the right.

Note 11. Only the *number* of rings, and not their size or distance from the centre, is taken into account. When the correct orientation is not immediately apparent, bisect the "horizontal row" by a horizontal axis and a vertical axis (as in XXI) and count the rings and fractions of rings in the four quadrants. If there is more than one combination of rings that could serve as the "horizontal row," apply the bisection in the other cases also (as in XXII). Choose the orientation that has as many as possible of the "remaining rings" in the upper right quadrant; if two or more orientations meet this requirement, choose the one of them that has as few rings as possible in the lower left quadrant. In the examples, phenanthrene (XVI) is shown correctly oriented with its single "remaining ring" turned upward toward the right; triphenylene (XVII) has one in the upper right quadrant and one in the lower right; Examples XVIII–XX show right and wrong orientations of chrysene; and

XXI and XXII show right and wrong orientations in a case that might not be immediately apparent.

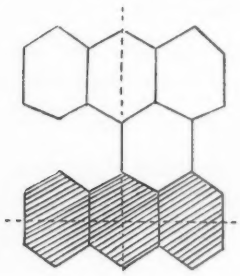
(XVII.)



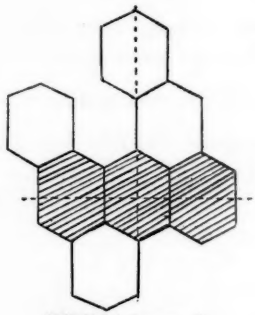
(XVIII.) (right)

(XIX.) (wrong)

(XX.) (wrong)



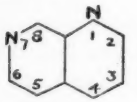
(XXI.) (right)



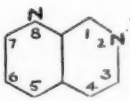
(XXII.) (wrong)

Rule 8. *Of orientations conforming to Rules 6 and 7, choose the one that gives the lowest numbers to hetero atoms when the formula is numbered as directed below (Rule 12).*

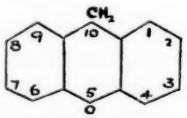
Examples :



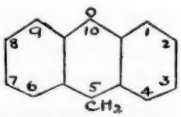
(XXIII.) (right)



(XXIV.) (wrong)



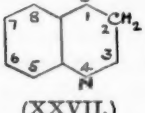
(XXV.) (right)



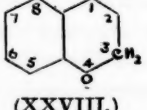
(XXVI.) (wrong)

Rule 9. *Of orientations conforming to Rules 6–8, choose the one that assigns low numbers to hetero atoms most nearly in the order of precedence given in Rule 2.*

Examples :



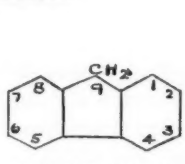
(XXVII.) (right)



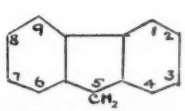
(XXVIII.) (wrong)

Rule 10. Of orientations conforming to Rules 6–9, choose the one in which unnumbered carbon atoms follow the lowest numbers possible.

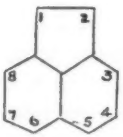
Examples: In XXIX the unnumbered carbon atoms follow the numbers 4,4,8,9; these are lower than the 4,5,9,9 of XXX. Similarly, the numbers 2,5,8 of XXXI are lower than the 3,5,8 of XXXII.



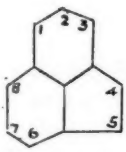
(XXIX.) (right)



(XXX.) (wrong)



(XXXI.) (right)

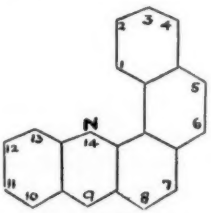


(XXXII.) (wrong)

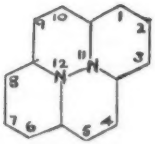
Rule 11. Of orientations conforming to Rules 6–10, choose the one that gives to hydrogen atoms the lowest numbers possible.

Rule 12. Number the oriented formula by beginning with the first free angle of the upper right ring and proceeding clockwise around the entire formula to the beginning, numbering all carbon atoms that are not common to two or more rings, and all hetero atoms. Number interior hetero atoms last of all, following the shortest path from the highest previous number.

Examples: (See also XXIII–XXXII)



(XXXIII.)



(XXXIV.)

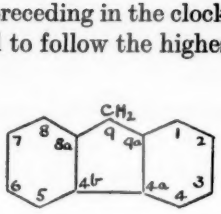
Note 12. The "first free angle" is the first angle, not also part of another ring, from which one may proceed clockwise around the ring.

Note 13. The "upper right ring" is the highest ring in the formula or, if two or more are equally high, then the ring farthest to the right in the highest row.

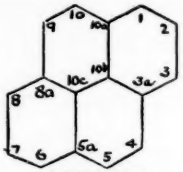
Note 14. Ordinarily, no numbers are needed for carbon atoms that are common to two or more rings. When such a need does arise, it is recommended that they be numbered by adding *a* (or *b*, *c*, etc., in case of a succession of them) to the number of the

position just preceding in the clockwise order; interior carbon atoms are considered to follow the highest number.

Examples :



(XXXV.)



(XXXVI.)

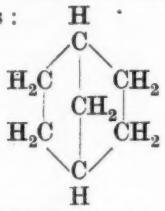
Note 15. Formulæ should always be represented in their correct orientation, because the maintaining of a fixed position is a valuable aid to memory. If one has a mental picture of the oriented formula, one can readily renumber it at any time by Rule 12.

C. The system does not belong to Classes A and B, and does not contain free spiro unions.

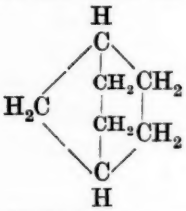
I. The system consists of two rings only, separated by either an atomic bridge or a valency bridge.

Note 16. Formulæ of systems belonging to Class C 1 must be drawn so that the bridge contains as few members as possible.

Examples :



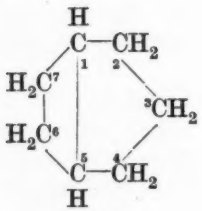
(XXXVII.) (right)



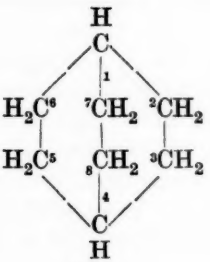
(XXXVIII.) (wrong)

Rule 13. Starting with one end of the bridge as 1, *number around the longer way to the other end of the bridge, then on around the shorter way to the beginning, and finally, by the shortest path, along the bridge itself if the bridge is atomic. If there are two or more possibilities for the shortest path, choose the shortest path from the highest previous number that will give a decision. Number all ring members.*

Examples :



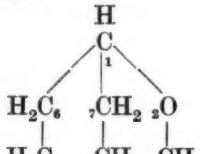
(XXXIX.)



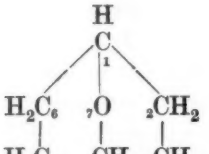
(XL.)

Rule 14. Of numberings conforming to the above rule, choose the one that gives the lowest numbers to hetero atoms.

Examples :



(XLI.) (right)



(XLII.) (wrong)

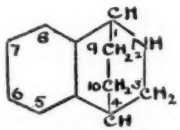
Rule 15. Of numberings conforming to the above rules, choose the one that assigns low numbers to hetero atoms most nearly in the order of precedence given in Rule 2.

Rule 16. Of numberings conforming to the above rules, choose the one that gives to hydrogen atoms the lowest numbers possible.

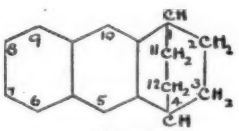
II. The system contains one or more atomic bridges the removal of which would throw the system into Class B.

Rule 17. Disregarding the atomic bridges and converting the resulting form to the lowest state of hydrogenation, number by Rules 6–12; then number the bridge members, following the shortest path as in Rule 13.

Examples :



(XLIII.)



(XLIV.)

Note 17. The atomic bridges in Class C II must contain as few members as possible and, the number of members having been determined, as few hetero atoms as possible. After the outside numbers have been determined by Rules 6–12, the formula must be so oriented that the ends of the atomic bridges receive the lowest numbers possible. For example, Formula XLIII is so drawn that the NH group is part of an outside ring and not of the bridge, so that it may receive as low a number as possible. In XLIV the bridge is shown between positions 1 and 4, not between 6 and 9.

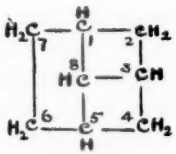
For conversion to the lowest stage of hydrogenation, see Note 2.

III. The system does not belong under I or II.

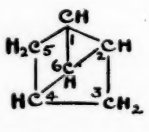
Note 18. The systems of Class C III contain two or more bridges, either atomic or valency. Special care must be taken to draw the formula so that the bridges shall be as simple and of as few members as possible. A branched bridge is regarded as consisting of a main bridge and one or more branch bridges. A branched bridge should be preferred to crossed bridges even though it contains more members (see XLVII and XLVIII), but in no case should the chain of bridge members between the two bridge ends be greater than either of the outside chains between the same points. In difficult cases it may be advisable to construct a spatial model so as to decide upon the most natural plane formula.

Examples :

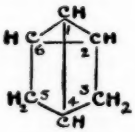
(XLV.)



(XLVI.)



(XLVII.) (right)



(XLVIII.) (wrong)

Rule 18. Select as the chief bridge (one end of which becomes position 1) the one having the most members or, if two have an equally large number of members, the one that divides the outside ring more symmetrically ; then number as in Rule 13 ; then number any remaining bridge members by the shortest path.

Examples : See XLV, XLVI, XLVII.

Note 19. If a branched bridge is present, part of it may constitute the chief bridge; for example, in XLVI, 1–8–5 is the chief bridge and 3–8 is the other bridge.

Rule 19. Of two or more numberings conforming to Rule 18, choose the one that gives the lowest numbers to the ends of the other bridges.

Example : See XLV.

Rule 20. If two or more numberings are possible in conformity with Rules 18 and 19, apply Rules 14–16.

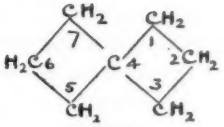
D. The system contains one or more free spiro unions.

I. The system contains spiro unions only.

Rule 21. Beginning with a ring member next to the spiro atom in the right end ring, number clockwise around the end

ring and on around the entire formula. Number all ring members.

Example :

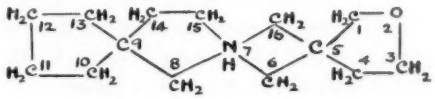


(XLIX.)

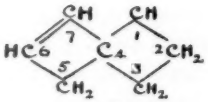
Rule 22. *Of two or more numberings conforming to Rule 21, choose the one that gives the lowest numbers to spiro atoms.*

Rule 23. *If there are two or more numberings conforming to Rules 21 and 22, apply Rules 14–16.*

Examples :



(L.)

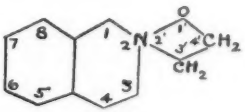


(LI.)

II. The system contains other ring unions in addition to spiro unions.

Rule 24. (*Provisional.*) *Treat separately each complex united by a free spiro union to another complex, giving to each the numbering it would have separately under the foregoing rules, but distinguishing the numberings from one another (as by primes). Give to the spiro atoms as low numbers in each complex as is consistent with the numbering of that complex.*

Example :



(LII.)

Comments.

Position of Double Bonds.—Opinions of chemists are divided as to whether saturated or unsaturated linkings should be given the preference in assigning low numbers. Usage in the past has apparently favoured one practice for certain classes of rings and the reverse for certain others. There seems to be a feeling that practice should be uniform and the Rules as now formulated favour saturated

linkings for low numbers in all classes. This number accords with such names as 1 : 2-dihydrobenzene, 1 : 2 : 3 : 4-tetrahydronaphthalene and 1 : 2-pyran, but not with such as 1-*cyclo*pentene and Δ^2-pyrroline.

To favour *un*saturated linkings for low numbers in all classes would, in the opinion of the author, be less satisfactory. The fact is, that in certain classes compounds are usually named on the basis of parent forms low in hydrogen (as with furan, anthracene), while in others the compounds are usually named on the basis of saturated parent forms. Hence in the former classes the names tend to give low numbers to hydrogen atoms (as with 1 : 2-pyran, 1 : 2-dihydroanthracene), while in the latter classes the names tend to give low numbers to double bonds (as with 1-*cyclo*pentene, 1-*spiro*heptene). The two systems overlap in such cases as 1 : 2 : 3 : 4-tetrahydrobenzene (1-*cyclo*hexene). Perhaps the Rules should recognise and embody this contrast. However, if chemists are willing to use such names as 4-*cyclo*pentene and 6-*spiro*heptene, or to adopt some other way of expressing the high numbers of the double bonds in these compounds, the present Rules ought to work satisfactorily. They at least have the merit of being simpler thus, but an ideal solution has not yet been attained.

Numbering of Classes A and B.—The principles employed in numbering systems of these classes are in general those used in M. M. Richter's "Lexikon der Kohlenstoffverbindungen" (see pages 14–26 of the introduction to the third edition); but inconsistencies have been eliminated and all hetero atoms are required to be numbered. Of the 311 numbered formulæ of Classes A and B given by Richter, 73 per cent. conform to the Rules; if Richter had numbered all hetero atoms, 88 per cent. would have conformed.

If the Rules are applied without exception, the commonly accepted numbering of a few well-known parent forms, including anthracene, phenanthrene, acridine, xanthene and purine, will have to be changed. Serious consideration has been given to introducing special rules in order to preserve some of these accepted numberings, and also to making outright exceptions of them. The overwhelming sentiment of organic chemists who have been consulted has, however, been in favour of keeping the Rules as simple as possible and making no exceptions. An elaborate attempt has been made by Stelzner and Kuh (see the 99-page article in the introduction to Vol. III of Stelzner's "Literatur-Register") to extend the principle of the commonly accepted numbering of anthracene and phenanthrene to other polycyclic systems. It leads to hopeless complications.

Definition of Class B.—This class includes the large majority of all known organic ring systems, and most of the compounds represented

by them are of the aromatic type. The definition is so drawn as to exclude such systems as norcarane, bi*cyclo*[3,1,0]hexane, etc., which are customarily numbered as systems of Class C. Any distinction between Classes B and C must be more or less arbitrary, but the line drawn in the Rules conforms fairly closely to actual usage. It would be more consistent to number the systems of Classes B and C alike and to include all ring members in the numbering, but this would run the numbers up very high in polycyclic aromatic compounds, and for the most part these additional numbers would not be used.

Numbering of Class C.—The method of numbering the bridged systems of Class C follows that of von Baeyer (*Ber.*, 1900, **33**, 3771–5), but extends it to cover many possibilities which von Baeyer did not attempt to consider. Class C II includes certain bridged systems (about forty are actually known) which are most conveniently numbered by treating them as Class B forms to which bridges have been attached.

Numbering of Complex Spiro Systems.—Rule 24 has been marked "provisional" because at some later time it may be thought desirable to give directions for numbering these systems, "straight around" like the preceding classes. No simple and certain way of doing this has as yet been worked out.

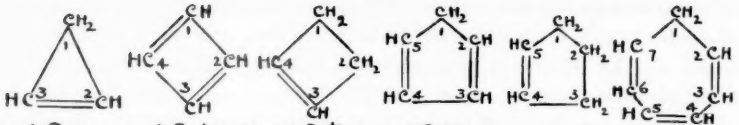
Additional Examples.

The following additional examples have been appended at the request of the International Committee for the purpose of showing more clearly the application of the Rules. In Classes C II and C III the chief bridge is denoted by a heavy line. "B_3" refers to Beilstein, 3rd edition; and "Richter" to M. M. Richter's "Lexikon" ("Ringsysteme" in Vol. I).

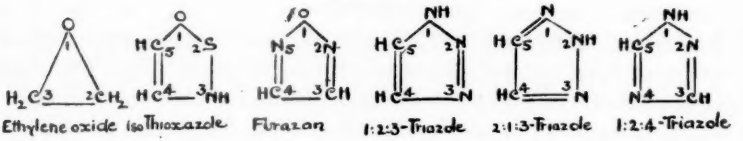
ADDENDUM.—The Publication Committee of the Chemical Society directs attention to three papers in the Journal of the Indian Institute of Science, Vol. 7, Part VIII, pp. 145–195 :

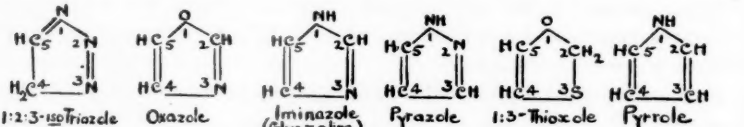
1. "The Systematic Nomenclature of Polycyclic Carbon Systems." By J. J. Sudborough.
2. "Polycyclic and Cage Systems of Carbon Compounds." By J. J. Sudborough and P. Ramaswami Ayyar.
3. "The Systematic Nomenclature of Heterocyclic Compounds including Polycyclic Structures." By J. J. Sudborough.

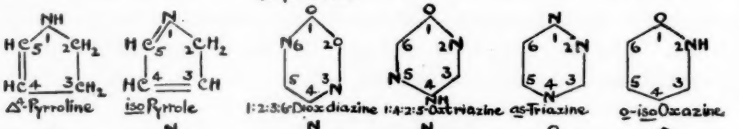
CLASS AI

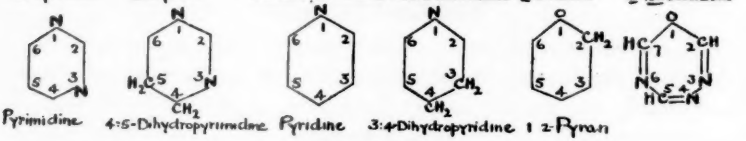


CLASS A II

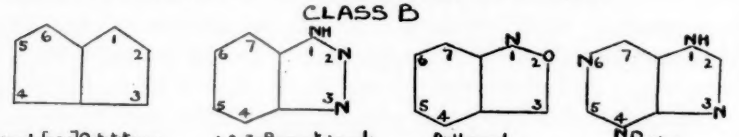


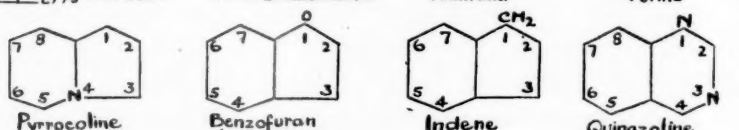


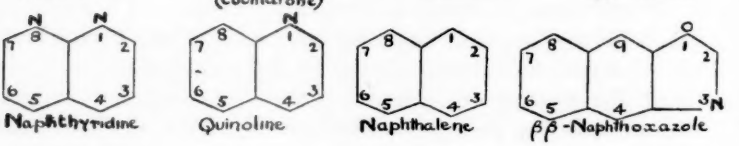


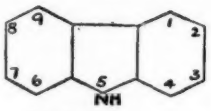


CLASS B

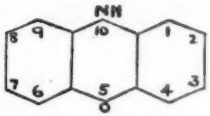




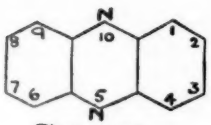




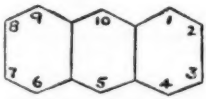
Carbazole



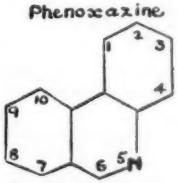
Phenoxazine



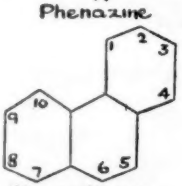
Phenazine



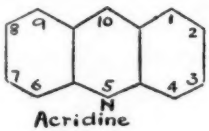
Anthracene



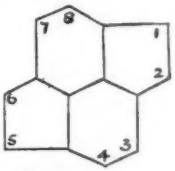
Phenanthridine



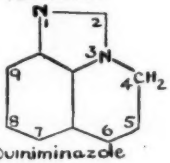
Phenanthrene



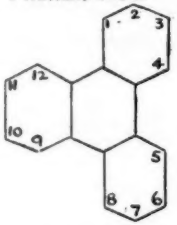
Acridine



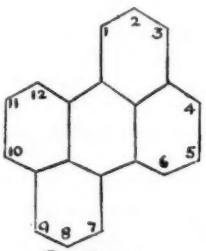
Pyracene



Quiniminazole



Triphenylene



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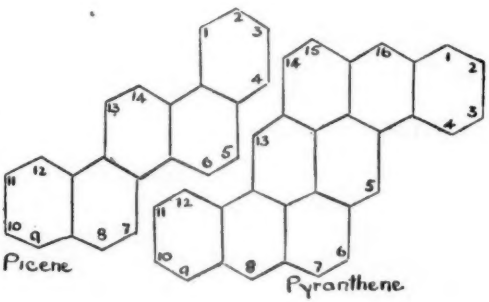

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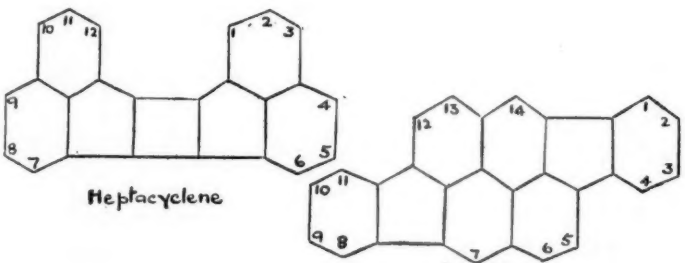
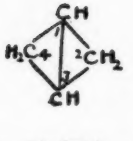


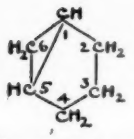
Heptacyclene

Mariene

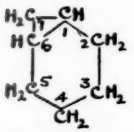
CLASS CI



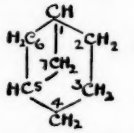
bicyclo[1,1,0]Butane.



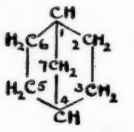
bicyclo[3,1,0]Hexane.



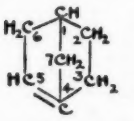
bicyclo[4,1,0] Heptane (Norcarane)



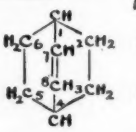
bicyclo[3,1,1]Heptane (Norpinane)



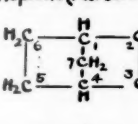
bicyclo[2,2,1]Heptane (Norcamphane)



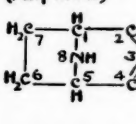
bicyclo[2,2,1]Hepta-ene.



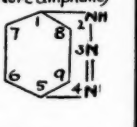
bicyclo[2,2,2] Oct-7-ene



B_3 IV, 715

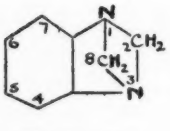


Nortropidine

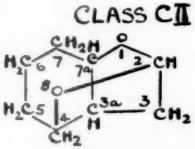


p-Benzene-diazoimide

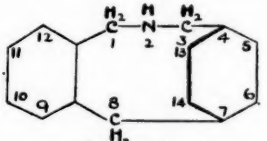
CLASS CII



B_3 IV, 567

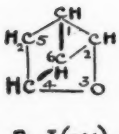


B_3 III, 596

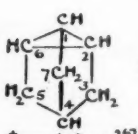


B_3, II (1096)

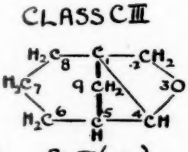
CLASS CIII



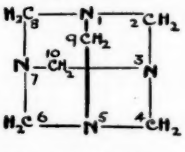
B_3 I(266)



tricyclo[2,2,1,0^{2,6}]-Heptane

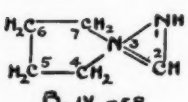


B_3 III (460)



Hexamethylenetetramine

CLASS DI



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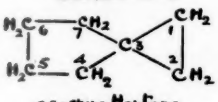
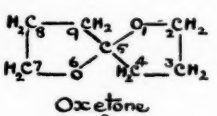
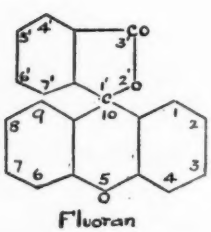


as-spiro Heptane

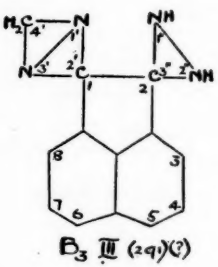


Oxetone

CLASS DII



Fluoran



B_3 III (291)(?)

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THE names of new compounds should be italicised (underlined in the typescript), and the results of analysis given in the form :

> (Found : C, 43·2 ; H, 6·5 ; N, 11·3 ; *M*, cryoscopic in benzene, 276, 258. $C_9H_{16}O_6N_2$ requires C, 43·5 ; H, 6·4 ; N, 11·3% ; *M*, 248).

Only in special cases should full analytical data be recorded.

For known compounds, the results of analysis should be given in the form :

> (Found : C, 50·1 ; H, 11·1 ; N, 39·1. Calc., C, 50·0 ; H, 11·1 ; N, 38·9%).

In giving references to other work, the journal (abbreviated title), the year, the volume, and the page should be given in the text in the order shown ; e.g. *J. pr. Chem.*, **1905**, **71**, 260. The official list of abbreviated titles is given at the end of the Annual Index of Abstracts.

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JOURNAL

OF

THE CHEMICAL SOCIETY.

I.—*The So-called Poisoning of Oxidising Catalysts.*

By Charles Moureu and Charles Dufraisse.

1. Davy (*Phil. Trans.*, 1817), in his remarkable investigations on flames, observed that certain combustible gases (especially olefiant gas) prevent hydrogen from burning in oxygen under the influence of an electric spark. Turner (*Edinburgh Phil. Journ.*, 1824, **11**, 99) and W. Henry (*Phil. Trans.*, 1824, Part II, p. 266), working independently, found that these same gases had the property of preventing the combustion of hydrogen in the presence of finely-divided platinum; this was the first observation of the "poisoning" of a catalyst. Faraday (*Phil. Trans.*, 1834, Part I, p. 71) repeated these experiments and extended them to other gases or vapours. Similar observations were made also by W. C. Henry (*Phil. Mag.*, 1836, [ii], **9**, 324). These phenomena are closely related to more recent observations, *e.g.*, the action of gases such as acetylene, hydrogen sulphide, and hydrogen phosphide, in hindering the catalytic oxidation of ammonia gas in the presence of platinum (Decarrière, *Compt. rend.*, 1921, **172**, 1663; 1921, **173**, 148; 1922, **174**, 460).

How should these phenomena be interpreted? Various hypotheses have been postulated, but, as Faraday justly observed, they are not satisfactory. The explanation which is most commonly given even now consists in supposing that there is a modification of the catalyst, although this idea was rejected by Faraday as a result of some very conclusive experiments. Indeed it is difficult to see any essential difference between the experiments of Davy, in which a spark was used, and those of Turner and Henry, in which finely-divided platinum was used as a catalyst. The same materials were used in both and the same hindering action was observed; it is therefore probable that the mechanism of the action is analogous in the two cases. Since, however, we cannot reasonably speak of

" poisoning " an electric spark, it is advisable to reject this term altogether, as tending only to perpetuate an erroneous idea of the true mechanism of the action. For the same reason, we may also reject the interpretation, which consists in supposing the formation on the surface of the catalyst of a protecting layer which would insulate it from the gaseous mixture. This explanation is not very satisfactory even for experiments with a catalyst, and it is meaningless in the case of Davy's work, with an electric spark and no catalyst. It is necessary, therefore, as Faraday has already insisted, to look for some other explanation.

2. We propose to interpret these phenomena by means of a theory developed by us in order to explain our own observations of the hindering of oxidation, which may be summarised as follows :

Certain compounds, if added in very small quantities to autoxidisable substances, prevent their autoxidation. We have named these compounds " antioxygenes " (*Compt. rend.*, 1922, **174**, 258). Compounds having one or more phenolic hydroxyl groups always possess this property toward a large number of autoxidisable substances, and sometimes to a very high degree; thus quinol, catechol, and pyrogallol are particularly active in this respect. In our opinion (*ibid.*, 1923, **176**, 624), the mechanism of this action is as follows : The antioxygenes act by decomposing catalytically the peroxide $A[O_2]$,* which results from the union of the autoxidisable substance with one molecule of free oxygen, O_2. The peroxide $A[O_2]$ oxidises the antioxygene B with the formation of the peroxide B[O], whilst it is transformed itself into another peroxide, A[O]. The two peroxides, A[O] and B[O], as they are antagonistic, mutually destroy each other (as has been observed in the case of a number of antagonistic peroxides) and thus regenerate the three molecules, A, B, and O_2, in their original state. The three equations below sum up our conception of the antioxygenic action :

$$A + O_2 = A[O_2]; \quad A[O_2] + B = A[O] + B[O]; \quad A[O] + B[O] = A + B + O_2.$$

Numerous conclusions may be predicted as a result of this theory, *e.g.* :

(i) Antioxygenic properties can belong only to oxidisable substances.

(ii) Antioxygenic properties should increase with the affinity of B for oxygen. There must, however, be an upper limit, which depends, among other conditions, on the ability of the autoxidisable substance A to be oxidised.

* The brackets are used to indicate that the oxygen is active.

(iii) Every oxidisable substance should show some antioxygenic properties, although the circumstances in which these are most strongly developed may vary according to the nature of the substance selected.

(iv) A given catalyst, B, should be able to function either as a positive catalyst or as a negative one, the direction of the catalysis being positive if the peroxide B[O] attacks the substance A in preference to the peroxide A[O], and negative if the converse conditions prevail :

$$A + O_2 = A[O_2];\ A[O_2] + B = A[O] + B[O];\ \begin{cases} \xrightarrow{\text{Positive Catalysis}} & B[O] + A = B + A[O];\ A[O] \longrightarrow \text{stable AO} \\ \xrightarrow{\text{Negative Catalysis}} & B[O] + A[O] = A + B + O_2 \end{cases}$$

In some cases, moreover, we must expect that the same catalyst may function sometimes as a negative, and sometimes as a positive catalyst, as a result of imperceptible variations of conditions.

It is well to add that this theory, which we have used as a guide in our researches for several years past, has not only enabled us to account for all the facts already known, but also to foresee others which, but for it, would have been entirely unexpected, *e.g.*, the catalytic properties of iodine and its compounds, of sulphur and its compounds, etc. (*Compt. rend.*, 1923, **176**, 797; 1924, **178**, 824, 1862). We consider that this theory can also account easily for the results obtained by Turner and Henry. We assume that the catalysis of the oxidation of hydrogen in contact with platinum occurs because of the formation of an unstable platinum oxide, $Pt[O_2]$. The gas which hinders this reaction may play the part of an antioxygene toward this transitory oxidation of the platinum, just as quinol, for example, plays the part of an antioxygene in the oxidation of benzaldehyde by interfering with the fixation of free oxygen by this compound. The catalysis may be represented by the following system of three equations, in which B represents the gas which prevents the reaction.

$$\begin{aligned} Pt + O_2 &= Pt[O_2] \\ Pt[O_2] + B &= Pt[O] + B[O] \\ Pt[O] + B[O] &= Pt + B + O_2 \end{aligned}$$

As the platinum oxide is destroyed catalytically as fast as it is formed, the platinum is thus deprived of its catalytic power of oxidation.

It could also be supposed that the platinum, acting as an oxygen carrier, oxidises the hydrogen and the interfering gas simultaneously

to form two antagonistic peroxides, which then are mutually reduced by each other, in conformation with the usual reaction.*

The so-called poisoning of the catalyst may therefore be in reality nothing but an antioxygenic action, just as in our experiments. In support of this point of view, it is important to observe that the gases indicated as having this hindering action are without exception oxidisable, as our theory requires. Indeed, W. Henry had already noted in 1824 (*loc. cit.*) that hindering properties were not to be found in "gases which do not combine with oxygen," and Faraday's researches fully confirmed this observation.

We consider that our theory applies similarly to the various cases of catalytic poisoning in oxidation phenomena.

As for Davy's experiment, we have here an ordinary antioxygenic action, as in our own experiments: the hydrogen is the oxidisable substance A and the interfering gas (ethylene, carbon monoxide, etc.) plays the part of the antioxygene B.

In conclusion, it is of interest to notice how complex may be the chemical phenomena which take place in a reacting mass, even although the final effect, the only one which we perceive, is relatively simple. We are, indeed, being compelled more and more to adopt the view that a chemical reaction is in reality made up of a series of transformations of different rapidities. Of these we observe only the final one, which corresponds to a stage possessing a greater stability than those preceding it.

LABORATOIRE DE CHIMIE ORGANIQUE,
COLLÈGE DE FRANCE, PARIS. [*Received, June 18th*, 1924.]

II.—*A Fractionating Column with Moving Parts.*

By JAMES ECKERSLEY MYERS and WILLIAM JACOB JONES.

CONSIDERABLE attention has been paid to the improvement of the fractionating column and to the question of its efficiency. The matter is fully treated in "Distillation Principles and Processes" by Sydney Young (London, 1922) and in the "Symposium on

* It has sometimes been observed that the catalyst appeared to have lost its catalytic activity after it had been subjected for a moment to contact with a reacting mixture contaminated with certain interfering gases, as in the case, for example, of contamination by hydrogen phosphide. Here we must admit that the interfering gas has caused the formation (by oxidation or by condensation or by reaction on the catalyst) of substances of small volatility, which remain fixed on the surface of the catalyst and must be destroyed in order that the catalytic activity (regeneration of the catalyst) may reappear. These substances then play the part of antioxygenes in accordance with the general mechanism explained above.

Distillation" (*J. Ind. Eng. Chem.*, 1922, **14**, 476—497). However, the columns therein described are of the usual type with stationary parts, and it was suggested to the authors by Professor Arthur Lapworth, F.R.S., that it would be of interest to construct a fractionating column with moving parts and to compare its performance with those of fractionating columns of the usual type.

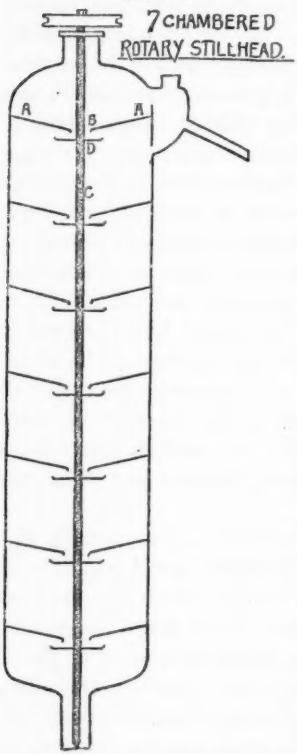
In the perfect fractionating column equilibrium between vapour and liquid would be attained at each point or in each section. For such an arrangement a necessary condition would be perfect contact between vapour and liquid at each point or in each section throughout the column. The more nearly this is approached in real practice, the greater will be the efficiency. In order to attain this, agitation of the vapour and a continuous fine dispersion of the liquid in each section of the column would be helpful, provided, of course, that the energy consumed in effecting these two operations was not excessive. In the case of an upright column of cylindrical or conical form, and consisting of several sections, the mechanically simplest way to effect fine dispersion of the liquid in each section is to provide the column with a central vertical revolving shaft, which within each section carries a horizontal and centrally-placed disk or cup, the function of the revolving disk or cup being to receive the liquid falling from the next higher section, and by centrifugal action to impel it either in the form of fine drops or as a thin film through the section.

In its flight the liquid comes into intimate contact with the ascending vapour in the section. After its flight the liquid falls in contact with the wall of the section, and finally, when it arrives at the aperture in the bottom of the section, drops down on to the revolving disk in the next lower section, where the process above described is repeated. In order to secure the greatest efficiency the duration of free flight should be considerable compared with the time occupied in falling in contact with the wall, and for this reason a cup form of impeller would in general be preferable to a disk one, as the former would give an initially upwardly-directed flight with a consequently lengthier trajectory for a given free horizontal range. However, in practice with the forms and dimensions of column and at the speeds of revolution which we have employed, we have found no advantage in the use of a cup form over a disk one. In this connexion it appears that it is neither the exact shape of the disk nor the speed of revolution of the shaft that matters so much as the peripheral velocity of the disks. Therefore, by using disks of greater diameter the same effect could be attained with a diminished speed of revolution of the shaft, and this would be a considerable engineering and economic consideration in the

practical employment of a rotary column, but in any case an adequate period of free flight must be given to the liquid.

Agitation of the vapour in each section could be effected by means of propeller blades, of suitable form and dimensions, fixed to the shaft and placed below the disk. In the experiments described below, however, we have not employed such a vapour-agitating device.

FIG. 1.



We have designed a fractionating column on the lines described in the foregoing. The column, a skilful piece of work by Mr. Stelfox of Manchester, was constructed of tinned copper, and was cylindrical in form, 32·5 cm. high and 7·5 cm. in diameter. It was divided into seven sections by downwardly-directed conical trays, A, which were equally vertically spaced at 3·5 cm., and the centres of which were circular horizontal apertures, B, 1·25 cm. in diameter. A shaft, C, made of thin iron rod, passed centrally through the apertures, and at its end at the bottom of the column worked on a bearing which was fixed to the column. Within each section the shaft carried a thin copper horizontal disk, D, 2·5 cm. in diameter. In order to secure the best working it is important that both column and shaft should be accurately vertically orientated. The shaft emerged out of the highest section by a fairly tightly stuffed passage, and, above, it carried a driving pulley. The highest section of the column was provided with a side exit-tube for the vapour, and near by was a thermometer to register the temperature of the escaping vapour. The whole column was protected from draught by an asbestos sheet.

In an experiment the liquid mixture to be fractionally distilled was contained in a copper boiling flask, which was attached by means of a cork to the bottom of the column. The driving pulley was attached to a motor and to a tachometer. The vapour issuing out of the exit-tube was condensed, collected in a receiver, and thereafter examined. Throughout all our trials a constant rate of collection of distillate was maintained, the heating being so controlled that about one drop of distillate fell per second into the

receiver. In our experiments the atmospheric pressure was sufficiently near normal to obviate any correction of boiling points on that account. By conducting our distillations under the described conditions, we were enabled directly to compare the results obtained with our column with those obtained with other columns on identical mixtures at the same rate of distillation. In each experiment, 200 c.c. of mixture were used. In the tables the following abbreviations are used. F T stands for the final temperature of the fraction, V for the volume of the fraction in c.c., V/D for the volume of the fraction per degree, T V for the total volume of distillate, and R for the number of revolutions of the shaft per minute.

Experiment A. The mixture consisted of equal parts by volume of benzene and toluene.

FT.	V.	V/D.	TV.	R.
82°	41	22·8	41	1100
84	40	20·0	81	1100
86	8	4·0	89	1200
88	7	3·5	96	1400
100	13	1·1	109	1400
108	12	1·5	121	1500
110	42	21·0	163	1500

Experiment B. The mixture consisted of equal parts by volume of benzene and toluene.

V.	V/D.	TV.	R.
81·0	45·0	81·0	1600
4·5	2·3	85·5	2400
6·0	3·0	91·5	2400
3·0	1·5	94·5	2400
6·5	0·5	101·0	2400
10·0	1·2	111·0	2400
20·0	10·0	131·0	2400

Comparison of these two experiments shows the effect which an increased speed of rotation, and therefore finer dispersion of the liquid in the column, has on the completeness of the separation into the constituents.

Experiment C. The mixture distilled contained 99 c.c. of ethyl alcohol and 101 c.c. of water. R = 1200.

FT.	V.	V/D.	TV.	FT.	V.	V/D.	TV.
79°	99	141·4	99	97°	1	0·1	106
80	3	3·0	102	99·8	3	1·0	109
87	3	0·4	105				

In experiment C, the first fraction contained 94% by volume of alcohol, and thus of the 99 c.c. of alcohol originally taken, 93 c.c. were recovered in the first fraction in one distillation.

In order to afford a comparison between the performance of the rotary column and other standard forms, we have drawn up the following table in which are given data concerning the fractional distillation of 200 c.c. of a mixture of equal parts of benzene and toluene, the distillate being collected at the rate of a drop per second. Under the name of each column is given, corresponding to each fraction, the value of V/D, namely, the volume of the fraction in c.c. divided by its temperature-interval in degrees. The most efficient column is that which gives the highest value to V/D

in the immediate neighbourhood of the boiling points of the pure constituents, and the lowest value elsewhere.

Final Temp. of Fraction.	Hempel Column. 58 cm.	Young 8-section Evaporator Column. 78 cm.	Rotary 7-section Column at 2400 Revs. 32·5 cm.	Young 13-section Evaporator Column. 131 cm.
82°	15·6	25·6	45·0	48·8
84	12·0	15·0	2·3	1·6
86	9·0	4·0	3·0	1·2
88	6·0	2·0	1·5	1·0
100	2·0	2·6	0·5	0·4
108	2·0	0·8	1·2	0·4
110	7·0	3·6	10·0	2·4

As will be seen from the above, the rotary column performed satisfactorily. Another point in its favour is that during the distillation it held a smaller mass of liquid and vapour than any of the other forms.

Owing to the complexity of the factors involved and to our incomplete knowledge of them, it is impossible to give exact directions for determining the real economic efficiency of any type of fractionating column except by direct trials. The best that one can do in the case of a new type is to compare its performance with that of a standard efficient type, paying attention to completeness of separation of the constituents of the mixture with which it has to deal, and to its initial and running costs. No claim is here made that we have established the best form, dimension, or revolution speed for a rotary column, nor, in view of our experience of the diverse behaviours of different mixtures, do we consider that such could be satisfactorily determined except by direct trials with the particular mixture that is to be resolved by distillation into its constituents. However, sufficient evidence has been adduced to demonstrate that the principle of the fractionating column with moving parts introduces a useful innovation, and one that might in certain cases be advantageously adopted in practice. We are at present designing a new model which it is hoped will be more efficient than the one here described.

We desire to thank Professor Lapworth for his suggestion and for his interest in the work.

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III.—*The Absorption Spectra of Various Aldehydes and Ketones and some of their Derived Compounds.*

By JOHN EDWARD PURVIS.

THE aim of this communication is to discuss the results observed in the following compounds: formaldehyde, paraldehyde, trithioformaldehyde, α-trithioacetaldehyde, β-trithiobenzaldehyde, α-diphenylglyoxime, diacetylmonoxime, acetal, methylal, benzylideneacetone, benzylideneacetophenone, benzylideneacetoxime, benzylidenedeoxybenzoin, benzylidenecamphor, cinnamylidenecamphor.

The methods of investigation have been described before. In 1912, the author and McCleland (J., **101**, 1810) and Bielecki and Henri (*Ber.*, **45**, 2819) investigated the absorption bands of various aliphatic aldehydes and ketones. Among these, solutions of formaldehyde in alcohol and in ether showed no selective absorption.

The following substances exhibit no specific absorption in solution. The concentration of the solution and the name of the solvent are given, and also the positions of the rays from a condensed cadmium spark that were transmitted through varying thicknesses of the solution, increasing by 2 mm. for each photograph (only the first and the last value are given in each case): *Formaldehyde*, 30% in water; 10 mm., λ 2250; 90 mm., λ 2930. *Paraldehyde*, 2*M* in ethyl alcohol; 12 mm., λ 2150; 90 mm., λ 2560. *Trithioformaldehyde*, *M*/550 (the highest obtainable) in ethyl alcohol; 20 mm., λ 2560; 60 mm., λ 2680; *M*/5500; 20 mm., λ 2160; 60 mm., λ 2270. *α-Trithioacetaldehyde*, *M*/10 in alcohol; 10 mm., λ 2650; 30 mm., λ 2750; *M*/100; 10 mm., λ 2500; 30 mm., λ 2600; *M*/1000; 10 mm., λ 2180; 30 mm., λ 2350. *β-Trithiobenzaldehyde*, *M*/1350 (the highest obtainable) in alcohol; 20 mm., λ 2570; 60 mm., λ 2750; *M*/13,500; 20 mm., λ 2290; 60 mm., λ 2450. *Methylal*, 2*M* in alcohol; 10 mm., λ 2100; 80 mm., λ 2190. *Acetal*, 2*M* in alcohol; 20 mm., λ 2550; 76 mm., λ 2750; *M*; 10 mm., λ 2450; 62 mm., λ 2570; *M*/10; 10 mm., 2310; 62 mm., λ 2470; *M*/100; 12 mm., λ 2120; 56 mm., λ 2270.

Purvis and McCleland showed (*loc. cit.*) that the vapour of formaldehyde exhibited a considerable number of narrow bands. Acetaldehyde has a solution band at 1/λ 3500 (λ 2856), and one large vapour band; chloral has a solution band at 1/λ 3430 (λ 2912), and chloral hydrate has no band, the solution being very transparent to the cadmium rays. To explain these phenomena, it is suggested that formaldehyde unites with the solvent, forming a compound whose formula might be represented as $H{\cdot}CH(OH)_2$ and is thus comparable with $CCl_3{\cdot}CH(OH)_2$. Again, if the formula of paralde-

hyde, which shows no absorption band, is written as (A), it may be suggested that a similar type of condensation occurs with

(A.) $CHMe\langle^{O\cdot CHMe}_{O\cdot CHMe}\rangle O$ (B.) $H_2C\langle^{O-CH_2}_{O-CH_2}\rangle O$

formaldehyde, and its constitution could be described as (B), and this again would explain the absence of specific absorption.

The solution of β-trithiobenzaldehyde showed there was no trace of the two solution bands of benzaldehyde described by Purvis and McCleland (J., 1913, **103**, 1088); and in this respect it is comparable with trithioformaldehyde described above.

The absence of any selective absorption in solutions of methylal and acetal may be explained by a consideration of their constitutional formulæ $H\cdot CH(O\cdot CH_3)_2$ and $CH_3\cdot CH(O\cdot C_2H_5)_2$. The aldehydic oxygen is fully saturated and there is no centre of vibration to give specific absorption.

α-Diphenylglyoxime.—The substance is not very soluble in alcohol, and the strongest solution available was *M*/1700. There appeared to be a very weak band at about λ 2380, corresponding to the very weak band of liquid diphenyl at λ 2300 described by Baly and Tryhorn (J., 1915, **107**, 1058). The following numbers represent some of the observations made between 20 mm. and 60 mm. thickness, increasing by 2 mm. for each exposure.

M/1700.	Thickness (mm.) ...	20	60			
	Rays transmitted to	λ 2750	2900			
M/17,000.	Thickness (mm.) ...	20	32	40	50	60
	Rays transmitted to	λ 2150	2270	2400 *	2550	2590

The weak band lies between λ 2400—λ 2270 in this solution.

* The stronger Cd lines round about λ 2300 were just visible.

Two solution bands of benzil are described by Baly and Stewart (J., 1906, **89**, 502) at 1/λ 3900 (λ 2563) and 1/λ 2650 (λ 3773), and Hantzsch and Schweite (*Ber.*, 1916, **49**, 213) describe a similar curve. Hantzsch (*Ber.*, 1910, **43**, 1651) found no definite band in *syn*-benzilmonoxime, although the line of absorption is bent a little in the region of 1/λ 2800—1/λ 3250 (λ 3569—λ 3075) and also in the region of 1/λ 4000 (λ 2498). The two benzil bands have completely disappeared in the glyoxime. The author can confirm the absence of selective absorption in diacetyldioxime first noticed by Baly and Stewart (J., 1906, **59**, 502).

Solutions of strengths varying from *M*/10 to *M*/10,000 of diacetylmonoxime were also examined, but no definite bands were noticed. The general absorption was fairly strong, for through 30 mm. of a *M*/10-solution the rays were absorbed from about λ 3850; through

30 mm. of a $M/100$-solution, from about λ 3370; and through 30 mm. of a $M/1000$, from about λ 2700.

It is clear, therefore, that α-diphenylglyoxime behaves like all oximes in this respect. In this substance, the two CO groups of benzil have been completely eliminated in the oxime, and the specific absorption of the original substance has been destroyed.

Benzylideneacetone.—The author has repeated the observations of Baker (J., 1907, **91**, 1490) and Baly and Schaefer (J., 1908, **93**, 1808) and confirms the presence of a large band at $1/\lambda$ 3500 (λ 2856). The author has also repeated the work on the absorption of acetone first described by Stewart and Baly (J., 1906, **89**, 492), and of benzaldehyde described by Purvis and McCleland (J., 1913, **103**, 1088). The absorption curves of these substances have been drawn (Fig. 1) for comparison with that of benzylideneacetone. The band of the latter substance is narrower than the acetone band, and the two benzaldehyde bands have disappeared.

The vapour of benzylideneacetone was examined in a 200-mm. tube at various temperatures and pressures with the following results:

$T°$.	Pressure in mm.	
50	792	The rays were transmitted to λ 2120.
60	802	The rays were weak between λ 2780 and λ 2420 and then transmitted to about λ 2120.
70	812	The rays were almost completely absorbed between λ 2880 and λ 2400 and then transmitted to λ 2150.
80	822	The rays were completely absorbed between λ 2950 and λ 2350 and then transmitted to λ 2200.
90	832	The rays were absorbed from λ 3000, but the series of Cd lines round about λ 2300 was visible.
100	842	The rays were absorbed from λ 3010, the Cd lines at λ 2300 being very faint.

Similar results were obtained when the vapour was examined at a constant pressure of 757 mm. and at temperatures varying from 40—80°. The radiations of a Welsbach light were used to investigate the more refrangible regions of the visible spectrum. No absorption bands were recorded, and the rays were transmitted to about λ 3200, *i.e.*, as far as the radiation affected the photographic plate. All these experiments prove that the narrow vapour bands of benzaldehyde described by Purvis and McCleland (*loc. cit.*) have disappeared. These authors also proved (*loc. cit.*) that acetone had no narrow vapour bands. The results appear to indicate that the different unsaturated vibratory centres do not act independently of each other. In this direction, the author has pointed out (J., 1914, **105**, 2482) that the solution and vapour of benzylidene chloride possess the residues of three benzene solution bands (comparable with the three toluene bands), and that

benzaldoxime has several of these residual bands bordering on a stronger band. The elimination of the oxygen of the CO group in both cases enables the molecule to recover some portion of the vibrations of the original benzene ring.

It was also shown (*loc. cit.*) that cinnamaldehyde had one large band covering the area occupied by the two benzaldehyde bands and that through 30 mm. of a *M*/10-solution the former substance absorbed the rays from λ 3940, *i.e.*, within the areas of the visible spectrum.

Now, in benzylideneacetone the two benzaldehyde bands disappear and the larger single band is not unlike the acetone band. Also through 30 mm. of a *M*/10-solution the substance absorbed the rays from about λ 3850, *i.e.*, within the borders of the visible region. There is no exhibition of any residual benzene bands noted in benzylidene chloride and benzaldoxime. It is apparent, therefore, that the vibrations of the three unsaturated centres of benzylideneacetone do not act independently. Their interacting oscillations produce great absorption and the development of a weak colour.

Cinnamylideneacetone has a large band at about 1/λ 3200 (λ 3120) according to Baly and Schaefer (J., 1908, **93**, 1808); and at the greatest thickness the line of absorption appears to be at about λ 3815, *i.e.*, at the edge of the more refrangible region of the visible spectrum. This large band is not unlike that of benzylideneacetone.

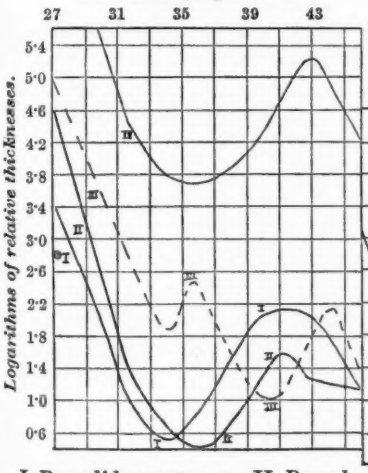
Benzylideneacetoxime.—Alcoholic solutions of this colourless substance were examined and the curve was drawn (Fig. 1). Comparing this case with benzylideneacetone, it is evident that the colour of the latter depends chiefly on the CO group. In the oxime the line of general absorption and the band are shifted more towards the more refrangible regions. The band is a little wider and less persistent and the substance less transparent in the more refrangible regions. The line of general absorption through 30 mm. of a *M*/10-solution is at λ 3500, and in benzylideneacetone it is at λ 3850.

Benzylidenedeoxybenzoin.—Solutions of this substance were examined and the curve (Fig. 2) shows one very shallow band, the line of general absorption rapidly extending into the visible regions. The line of general absorption through 30 mm. of a *M*/100-solution was at λ 3930. Stobbe and Ebert (*Ber.*, 1911, **44**, 1289) describe a large band in benzylideneacetophenone. The author has repeated the observations and drawn the curve for comparison. The band is wider than that of benzylideneacetone and is shifted more towards the red end.

Cinnamylidenecamphor.—Lowry and Southgate (J., 1910, **97**,

905) describe a solution band of benzylidenecamphor at about $1/\lambda$ 3450 (λ 2896). The author has repeated these observations, to compare the phenomena with those exhibited by cinnamylidenecamphor (Fig. 2). The differences are the greater shift of the absorption of the latter towards the red, the lessened transparency of the cinnamylidene compound in the more refrangible regions, and the wider band. The chief effect seems to be that the additional unsaturated centre has strengthened the colour and shifted the band more towards the red. The line of absorption through 30 mm. of $M/10$-solution is at λ 3960 in benzylidenecamphor and at λ 4250 in cinnamylidenecamphor.

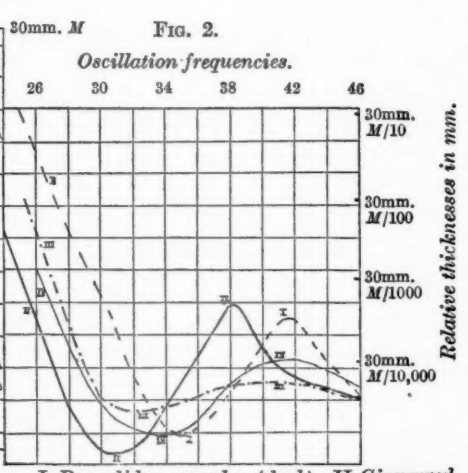
FIG. 1.



I *Benzylideneacetone*; II *Benzylideneacetoxime*; III *Benzaldehyde* (*dash*); IV *Acetone*.

30mm. *M*

FIG. 2.



I *Benzylidenecamphor* (*dash*); II *Cinnamylidenecamphor*; III *Benzylidenedeoxybenzoin* (*dot and dash*); IV *Benzylideneacetophenone*.

The outstanding results of these and earlier observations are: (1) all aldehydes and ketones exhibit selective absorption in well-defined areas of the ultra-violet region and this disappears when the aldehydic or ketonic groups are eliminated or neutralised. Examples of such phenomena are the oximes, paraldehyde, formaldehyde, thioaldehydes, methylal, acetal, chloral hydrate. (2) All other substances which have unsaturated centres also show specific absorption. These centres may be ethylenic or acetylenic or both, and may also act in union with other centres such as unsaturated benzene residues, ketones, and aldehydes. When these oscillatory centres are successively eliminated the absorption band or bands are altered in appearance; or the specific bands characteristic of

one or other of the remaining centres are partly developed. There is also a shift of the line of general absorption, and of the remaining band or bands, towards the more refrangible regions. Finally, when all the oscillatory centres are completely saturated, the substance shows no specific absorption and is very transparent. (3) The colour of organic substances, as Dr. Armstrong pointed out long ago, appears to depend largely on the substances possessing at least three unsaturated constituents. Each centre has its own specific influence which is unlike that of the others but with which it acts in co-operation. Substances which have at least three unsaturated centres and are coloured are benzylideneacetone, benzylideneacetophenone, benzylidenedeoxybenzoin, cinnamylideneacetone, cinnamylideneacetophenone, benzylidenecamphor, cinnamylidenecamphor. On the other hand, diacetyl and glyoxal are coloured and they have only two centres. It is suggested that the complete action of the unsaturated centres depends on their chemical type. It can hardly be doubted, for example, that a ketonic or an aldehydic centre exercises more influence in specific absorption than any other.

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CAMBRIDGE. [*Received, September 1st*, 1924.]

IV.—*The Ignition of Gases. Part V. Ignition by Inductance Sparks. Mixtures of the Paraffins with Air.*

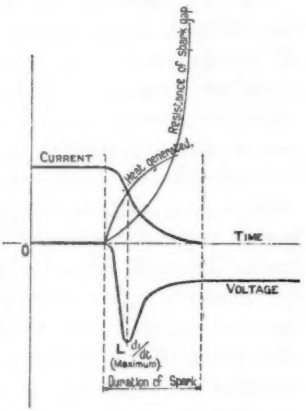
By RICHARD VERNON WHEELER.

ONE object of this part of the research on the ignition of gases was to compare the relative ignitibilities of mixtures of methane and air by inductance sparks (low-tension "break-flashes" or momentary arcs) with the values obtained when capacity sparks (high-tension impulsive discharges) were used as described in J., 1920, **117**, 903. For, as a source of ignition of gaseous mixtures, an inductance spark (produced when an electric current in an inductive circuit is interrupted by the separation of metallic contacts) differs from a capacity spark mainly in its longer duration, the difference being sufficiently wide to make it of importance to discover whether inductance sparks can be regarded, with capacity sparks, as "momentary" sources of heat (see J., 1924, **125**, 1858), or whether they more nearly approach in character "sustained" sources, such as heated surfaces (see *ibid.*, p. 1869).

The character of inductance sparks is most susceptible to changes

in the conditions under which they are produced, so that considerable variation can exist in their incendivity. Fig. 1, constructed mainly from oscillograph records, represents the variations, with time, of current, resistance, voltage and total heat generated in an inductance spark-gap produced by the rapid separation of metallic contacts. As the area of contact, anterior to rupture of the circuit, decreases, the electric resistance at that point increases and heat is generated. Eventually, the last remaining points of contact become so hot that the metal volatilises and, at the actual moment of break of circuit, a conducting band of metallic vapour is produced. This band rapidly increases in length as the fracture is widened, until the spark can no longer be maintained. With a spark of this general character, just capable of igniting a given inflammable mixture, ignition most probably occurs towards the end of its duration, but the precise moment depends upon the exact character of the spark as determined by the rate of increase of resistance and of decay of current in it. For these reasons, in any attempt, such as is made in this research, to determine the relative ignitibilities of different gaseous mixtures by means of inductance sparks of different intensities, we must recognise not only the changes, measured or deduced, purposely made in the intensity, but also the changes in the character of the sparks. These changes in character may be either inadvertent (as when the condition of the metallic surfaces that are separated changes) or a necessary concomitant of a change in intensity (as when the inductance of the circuit is purposely altered).

FIG. 1.



In the production of inductance sparks there are six chief variables, which can be divided into two groups according as they relate to (*a*) electrical or (*b*) mechanical conditions. In the former class are: (1) The self-inductance of the circuit; (2) the impressed voltage; and (3) the current flowing in the circuit before rupture. The latter class includes: (4) The nature of the metal at the spark gap; (5) the rate of break of circuit; and (6) the area of contact at the moment of break. Each of these variables can be more or less effectively controlled independently and the influence of each can therefore be determined. The most difficult to control and of which to gauge the influence is the last-named, and most of the

experimental difficulty of this work has been in maintaining constancy of this factor. For with the production of a spark there is a change in the condition of the surfaces at which it passes and with a readily oxidisable metal the change may be sufficient to alter considerably the area of contact available for successive sparks, as was observed when the influence of different metals at the spark gap was studied. Platinum or gold surfaces were found to be least susceptible to change and the former have been used for the majority of the experiments. Three different types of apparatus, each of which had its advantages for particular series of experiments, have been used. These are described in the experimental portion of this paper and are referred to as A, B and C.

Electrical Conditions.

With an inductive circuit carrying continuous current, the energy that should, theoretically, appear in the break-flash is the amount of energy stored electromagnetically in the system and should therefore amount to $\frac{1}{2}Li^2$. This expression does not, however, take into account losses in the circuit or absorption at the sparking-points, and although it might be permissible to express the relative incendivities of sparks produced under constant circuit conditions (with a given apparatus) by their energy values, it would be misleading to suggest a comparison of these values with others obtained under different circuit conditions and with a different apparatus for producing the sparks. The relative ignitibilities of different gaseous mixtures are therefore expressed in this paper simply by the values of the currents (in amperes) flowing in the circuit at the moment of interruption which yielded an inductance-spark just capable of causing ignition.

(1) *The Inductance of the Circuit.*—A number of inductances of known magnitudes were prepared, consisting of coils of silk-covered copper wire wound on cores of wood so as to be of constant value at all currents. These were introduced into the circuit from a battery of dry cells and the current at 90, 60, and 30 volts required for the ignition of different mixtures of methane and air by a break-flash at platinum contacts was determined, using apparatus A, which enabled a rapid break of circuit to be obtained. A number of the results are shown graphically in Fig. 2, in which percentages of methane are plotted against igniting-currents, each curve being for a given value of inductance and impressed voltage of the circuit. From the values used in the construction of these curves, the relationship between the igniting current for a given mixture and the inductance of the circuit can be determined. Thus Fig. 3 shows the relationship when mixtures containing 6·0, 7·0, and 8·0% of methane

were used and the impressed voltage was 90; additional values used for these curves are the igniting-currents when the inductance was 0·00815 henry, namely 1·52, 1·18, and 0·94 amp. for the 6·0, 7·0, and 8·0% mixtures, respectively. The relationship, between the values of L of 0·008 and 0·095 henry, can be expressed by the equation $Li^{1\cdot4} = k$; that is to say, the energy required in the circuit before break ($\frac{1}{2}Li^2$) to produce the igniting sparks was nearly constant. This result is deceptive, however, for in other series of experiments, carried out with a different method of producing the sparks, the value $\frac{1}{2}Li^2$ was by no means constant. (In this con-

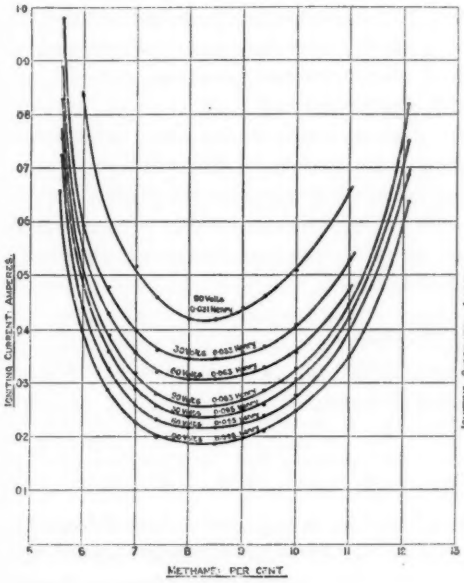


FIG. 2.

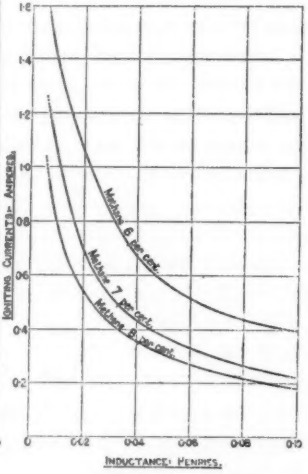


FIG. 3.

nexion, see Morgan, J., 1919, **115**, 24). A simple law connecting i with L in ignition experiments could only be expected if sparks of the same character could be produced with different values of L, and it would appear not to be possible to vary the intensity of a spark (by varying the inductance) without altering its character; for at any particular instant during a break-flash, when L is the inductance of the circuit, r the resistance of the spark-gap, R the resistance of the rest of the circuit, and V the impressed voltage, the value for the current is $(V - Ldi/dt)/(r + R)$, whilst its limiting value at the outset is V/R.

(2) *The Impressed Voltage.*—In general, it can be stated that the amount of current in the circuit is of far greater importance than

the impressed voltage as regards the igniting power of the flash produced on breaking the circuit. Especially is this so with highly self-inductive circuits. Thus an 8·0% methane–air mixture was ignited by the break-flash with a current of from 0·24 to 0·25 ampere under the conditions of the experiments at any voltage between 10 and 30, the self-induction of the circuit being 0·095 henry. With higher circuit voltages, however, the igniting current decreases, as the results recorded in Fig. 2 show. When the contacts at which the break-flash is produced are together, the voltage drop between them is zero; as soon as they are completely separated, the voltage between them is equal to the impressed voltage. During the separation of the contacts two actions are tending to make the arc between them persist, namely, the induced voltage, which progressively diminishes, and the impressed voltage, which progressively increases. If the impressed voltage is high, it will contribute materially to the maintenance of the arc. This effect is more marked when the rate of separation of the contacts is comparatively slow, so that the value of the induced voltage (Ldi/dt) is low. For example, a series of experiments using apparatus B, in which massive electrodes of platinum are drawn apart slowly, gave the results shown in Table I.

TABLE I.

Ignition of a 7·8% *Methane–Air Mixture. Inductance of Circuit* 0·095 *henry.*

E.M.F. (volts)	25	40	60	70	80	90	110	140
Igniting current (amps.)	1·18	1·00	0·80	0·73	0·66	0·60	0·50	0·38

It is evident that the energy of the sparks, as deduced from the expression $\frac{1}{2}Li^2$, does not give a true measure of their incendivity; as is also apparent from the fact that the igniting currents for the same mixture of methane and air (7·8%) as determined in the two apparatus A and B, with the same circuit conditions before break (*e.g.*, voltage 90 and inductance 0·095 henry) is markedly different.

(3) *The Current.*—We have to consider the effect of using alternating instead of continuous current. Thornton, in his researches on the ignition of gaseous mixtures by inductance sparks (*Proc. Roy. Soc.*, 1914, **90**, *A*, 272), has employed alternating currents at various frequencies and voltages, and, so far as the ignition of mixtures of methane and air is concerned, has recorded that much larger currents are required to produce ignition than with direct current. For example, under the conditions of his experiments, the igniting current for a 9·5% methane–air mixture was 0·5 ampere with continuous current at 200 volts (inductance of circuit not stated),

whilst with alternating current at 200 volts and 100 periods per second it was 20 amperes root-mean-square (r.m.s.) value (or 28 amperes crest value), although the arrangement of the resistance and inductance of the circuit is stated to have been the same as that used for the experiments with continuous currents. Similar wide differences with alternating current at lower voltages and frequencies are recorded by Thornton.

To check this remarkable result, duplicate series of experiments were made with apparatus A, using (*a*) continuous current at 35 volts with 0·095 henry inductance and (*b*) alternating current at 25 volts r.m.s. value (35·3 volts crest value) with 0·098 henry inductance, 50 periods per second. The break-flashes were produced between contacts of platinum. In the experiments with alternating current, the procedure was to produce a series of 50 sparks (with a given current) at 5 seconds' interval in a charge of the mixture of methane and air undergoing test. If no ignition occurred, a fresh charge of mixture was admitted to the explosion vessel and a further 50 sparks were passed with the current value increased by 0·01 ampere. This process was repeated until ignition occurred, when the current value was reduced by 0·01 ampere and two or three hundred sparks were passed in several charges of the mixture to ensure that the least igniting current had been determined. The reason for this procedure, which was unnecessary with continuous current (although it was followed in several of the trials in order to make the comparison exact), was that it was impossible to arrange that the break-flash should be produced always when the current was at the crest of its cycle. Ignition was, in fact, more "difficult" with alternating current, because the production of a spark at the crest value of the current was a matter of chance. The lowest current at which ignition could be obtained was not, however, much different from that required when continuous current was used. Typical results are recorded in Table II.

TABLE II.

Ignition of Methane-Air Mixtures using (a) *Continuous and* (b) *Alternating Current* (50~). *Voltage* 35. *Inductance* 0·095 *henry.*

Methane %	6·15	7·10	7·60	8·00	8·50	9·00	9·60	10·20	10·90
Igniting current (amps.). Continuous	0·43	0·30	0·26	0·24	0·24	0·25	0·28	0·32	0·42
Alternating (crest values)	0·49	0·36	0·30	0·26	0·24	0·25	0·26	0·30	0·44

It was anticipated that, under certain conditions, rather more current would be required in the break-flash to ignite a given

mixture when the source of supply was alternating than when it was continuous, for the reason that the rapidly changing value of the former might shorten appreciably the duration of the transient arc, and the fact that the values for the igniting currents of the mixtures containing the lower percentages of methane are rather higher with alternating than with continuous current is probably due to this effect.

Mechanical Conditions.

(4) *The Nature of the Metal at the Spark-gap.*—Since an inductance spark is of the nature of a transient arc, current being conducted across the gap through the vapour of the metal, it would seem probable that the lower the volatility of the metal conductor the lower would be the igniting current for a given mixture, other conditions being constant, for less energy would be expended in forming a path for the current, or that path might remain open during a longer interval of time.

Several series of experiments to determine this question were made using apparatus C, which was designed to allow of the ready interchange of contacts of different metals whilst preserving as nearly as possible all other experimental conditions constant. The results are summarised in Table III. Mixtures of methane and air containing between 8·35 and 8·55% of methane were used and the inductance of the circuit was 0·03175 henry.

TABLE III.

Igniting Currents with Contacts of Different Metals. (Mixtures of Methane and Air).

		Igniting current. Ampere.			
		First series.			Second series.
Metal.	Boiling point.	At 80 volts.	At 100 volts.	At 120 volts.	At 120 volts.
Cadmium	778°	—	—	0·22	0·23
Zinc	918	0·34	0·26	0·23	0·25
Aluminium	1800	—	—	—	0·30
Silver	1955	0·44	0·41	0·38	0·32
Tin	2270	0·66	0·53	0·45	—
Copper	2310	—	—	0·49	0·38
Nickel	2330 ?	0·63	0·58	0·55	0·39
Iron	2450	0·58	0·52	0·49	0·42
Platinum	2450 ?	0·65	0·56	0·48	0·48
Gold	2530	0·86	0·59	0·50	0·34

The determinations presented considerable difficulty, for not only was it necessary to ensure that the area of contact between the poles at the moment of separation was the same in parallel experiments with different metals (a matter requiring fine adjustment of the apparatus), but with all the metals except platinum

and gold the production of a single spark sufficed to oxidise the surfaces to a greater or less degree (thus altering the area of metallic contact) so that in most instances it was necessary to repolish the surfaces between each break-flash.

In Table III the metals have been arranged in order of their boiling points (as recorded in Kaye and Laby's "Physical and Chemical Constants," 1921) and it is clear that there is a close relationship between those values and the "igniting currents," under standard electrical conditions, of a given mixture of methane and air. The energy available at break is utilised mainly in producing an arc of volatilised metal, and a given quantity of energy presumably produces an arc of short duration if the metal has a high boiling point and an arc of longer duration when the boiling point is relatively low. The duration of the break-flashes with the metals that gave the highest and the lowest results for the igniting currents (gold, platinum, zinc, and cadmium) were determined by photographing them on a rapidly revolving plate. The results are recorded in Table IV.

TABLE IV.

Duration of Break-flashes that Causes Ignition of an 8·5% Methane–Air Mixture.

Metal.	Relative Igniting-current at 120 volts. Ampere.	Duration of Break-flash. Second.
Cadmium	0·23	0·00321
Zinc	0·25	0·00234
Platinum	0·48	0·00081
Gold	0·50	0·00070

Thus, under standard conditions, a break-flash between cadmium surfaces with a current of 0·23 ampere flowing in the circuit before interruption lasts four times as long as one between platinum surfaces with a current of 0·48 ampere, a fact which no doubt accounts mainly, if not entirely, for both sparks having the same incendivity although the amounts of energy in the circuit at their moments of formation are so different.

In this connexion, reference may be made to determinations by v. Lang (*Wied. Ann.*, 1887, **31**, 384) of the minimum arcing potential, using poles of different metals, for although his results refer to maintained arcs, which the break-flashes are not, they give a measure of the degree of ease with which such arcs can be produced. The values depended essentially upon the distance apart of the poles and the current flowing in the circuit, and could be expressed by a formula $p = a + bli$, in which p is the observed *P.D.* in volts between the poles, l is the distance apart of the poles in mm., and i is the current in amperes, b being a constant (independent of the

current) and a the *E.M.F.* required to maintain the arc. Taking the somewhat arbitrary values of 0·5 ampere for i and 0·5 mm. for l, as lying within the range of the experiments recorded in Table III, v. Lang's determinations were: Cadmium, 10·9; zinc, 20·0; silver, 20·0; copper, 24·0; iron, 25·2; nickel, 26·4, and platinum, 27·8 volts, showing that the ease with which the arc is maintained is directly connected with the volatility of the metal.

(5) *The Rate of Break of Circuit.*—Since the incendivity of the break-flashes depends in part on the inductance voltage and since the magnitude of the inductance voltage depends on the product of the coefficient of self-induction L and the rate of change di/dt of the current in the circuit, it follows that the rate of break of the circuit—the speed at which the metallic contacts are separated—affects the incendivity of break-flashes produced under otherwise identical conditions. This is demonstrated qualitatively by experiments made with apparatus C, using platinum electrodes, which showed that the igniting-current for a given mixture of methane and air was 0·24 ampere when the rate of break was "rapid" and 0·60 ampere when it was "slow," other conditions remaining constant.

(6) *The Area of Contact at the Moment of Break.*—Since the production of a break-flash depends essentially on the temporary provision of a path for the current through a band of metallic vapour, it follows that the incendivity of a spark produced under otherwise identical conditions will be affected by changes in the area of metallic contact at the moment of break; for the smaller the area of contact at the instant of rupture the more readily will the mass of metal that then remains to form a conductor be turned into vapour that can continue the conduction, and the smaller the volume of vapour thus produced the greater will be the amount of energy concentrated in it and the greater, in consequence, will be its incendivity. Experiments (made with apparatus C) using pole pieces, of platinum, of different cross-sectional area with their surfaces carefully polished and aligned showed that a lower igniting-current was required for a given mixture of methane and air (under otherwise identical electrical conditions) the smaller the area of the poles.

Further information on the effect of the area of contact at the moment of break was obtained when the poles were made of a readily oxidisable metal, such as zinc, for then, unless the surfaces were repolished between each spark, the igniting current regularly decreased to a minimum (at which sparking ceased) as oxidation proceeded; presumably because the coating of oxide gradually reduced the area of metallic contact.

From the fact that so many factors, each having considerable influence on the character of the sparks, have to be taken into account, it will be realised that repetition of the results of apparently parallel experiments was by no means easy to obtain. No success attended experiments in which the break of circuit at which the flash occurred was made by hand; it was only by rendering all possible operations mechanical and automatic that any degree of consistency in the igniting currents could be secured, and during the course of each series of experiments repeated checks had to be carried out with a standard mixture (8·5% of methane in air) under standard conditions to ensure that no unnoticed change had taken place in the condition of the contacts.

From this study of the electrical and mechanical conditions necessary to produce inductance sparks of uniform character, it appeared that the optimum conditions were obtained if: (*a*) The battery voltage was low and the inductance fairly high, so as to ensure that the sparks should be maintained primarily by the inductance voltage; (*b*) the metal contacts at which the sparks were formed were not readily oxidised; (*c*) the rate of separation of the contacts was rapid; and (*d*) the area of contact at the moment of break was small. Comparative series of experiments were made with mixtures of each of the paraffins, methane, ethane, propane, butane, and pentane, with air, using continuous current at 30 volts with 0·095 henry inductance. The sparks were formed between contacts of platinum in apparatus A, which was judged to provide the optimum mechanical conditions for the production of sparks of uniform character.

The curves relating percentage of inflammable gas in the mixtures with air to " igniting-currents " were similar, with each hydrocarbon, to those obtained when secondary discharges (capacity sparks) were used as the means of ignition (see J., 1924, **125**, 1860) save that, in each instance, differentiation between the more readily ignitible mixtures was not so marked. The same differences in the degree of ignitibility of the paraffins was also observed, but again the differences were not so marked. The essential data are given in Table V.

The general result of these experiments is to show that, so far as the paraffin hydrocarbons are concerned, inductance sparks can be considered similar in effect to capacity sparks as means of ignition, despite the wide difference there is in the two types both as regards duration and volume. The longer duration and larger volume of the inductance sparks apparently have the effect of masking small differences in the ignitibility of those mixtures that are most readily ignited.

TABLE V.

Mixtures of the Paraffins with Air.

Combustible gas.	Mixtures most readily ignited by secondary discharge. (J., 1924, 125, 1863.) Per cent.	Relative igniting currents. Secondary discharge. Ampere.*	Mixtures most readily ignited by inductance sparks. Range. Per cent.	Mean. Per cent.	Relative igniting currents. Inductance sparks. Ampere.
Methane	8·3	0·59	7·8—9·0	8·4	0·24
Ethane	6·7	0·47	6·0—6·8	6·4	0·15
n-Propane	5·1	0·36	4·8—5·4	5·1	0·12
n-Butane	4·2	0·48	3·8—4·4	4·1	0·15
n-Pentane	4·0	0·52	3·6—4·2	3·9	0·23

* Currents in the primary circuit (see J., 1920, **117**, 903.)

EXPERIMENTAL.

Apparatus A (Fig. 4). A brass rod passing through the side of a spherical glass vessel of 100 c.c. capacity carried at its end a pointed strip of platinum, A, to form one of the electrical contacts at which the inductance spark should be produced. The other contact was a platinum rod, B. This rod was mounted on a glass support which passed through the ground-glass bearing, C, and could be caused to revolve by means of the pulley, D, driven by an electric motor. The glass support was hollow so as to enable electrical connexion to be established (by means of a copper wire, *E*, passing through it) between short pieces of thick platinum wire fused into either end. The upper platinum wire carried the contact rod, B, and the lower wire dipped into a mercury-cup, F, whence the electric circuit could be completed. The rod was revolved at such a speed as to make contact every 5 seconds with the strip, which was bent at an angle (in a manner not apparent from Fig. 4) so that the rod as it revolved remained in contact with it during about half a second and then released it suddenly, forming a quick break of circuit.

Apparatus B (Fig. 5).—The poles were cones of platinum fused into hollow glass supports which passed through ground glass bearings on opposite sides of a glass globe of 100 c.c. capacity. One support, A, was held by light springs (which allowed it a small amount of movement) so that the platinum pole was normally at the centre of the globe. The support, B, was attached to a strong spring, C, which could pull it half-way through the bearing.

A revolving cam (not shown in the diagram), acting on the rod, D, pushed this support against the pull of the spring so that its platinum pole made contact periodically with that of A. Electrical connexions were made through copper wires passing within the hollow

supports as in apparatus A. The cam was revolved by an electric motor at such a speed that contact between the poles was made and broken every five seconds and the arrangement was such that contact was maintained during half a second.

Apparatus C (Fig. 6).—This apparatus was similar in design to one used by Thornton (*The Electrician*, Sept. 8th, 1916). A small solenoid, A, was supported within a cylindrical explosion vessel of glass of 100 c.c. capacity. Its plunger carried one of the poles, a rod 0·5 mm. in diameter. The other pole, 1·5 mm. in diameter, was carried on a fixed support, B. The pole pieces were

FIG. 4.

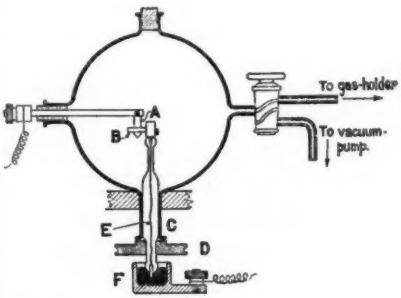
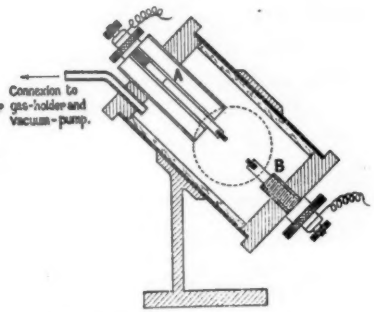


FIG. 6.



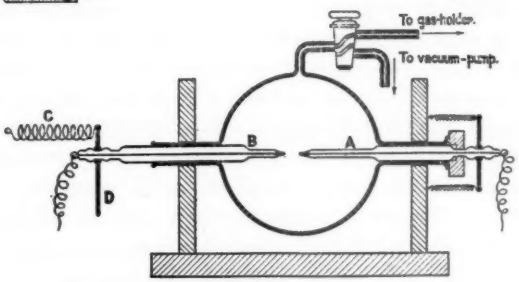


FIG. 5.

removable so that different metals could be used. When the solenoid was out of action, its plunger dropped so that the end surface of the pole attached to it rested on that of the fixed pole, but on passing an electric current through the coils the plunger was rapidly withdrawn so that a quick break of circuit occurred at the surfaces of the poles. Make and break of electric circuit in the solenoid (the electrical connexions to which are not shown in the diagram) were made automatically so that the poles were separated every five seconds.

Each apparatus could be evacuated so as to enable gaseous mixtures of known composition to be introduced. The mixtures

were stored in glass gas-holders over glycerol and water and were analysed before use. In each series of experiments, the electric circuit included a Post Office resistance box (the coils of which were non-inductively wound) to enable small changes of current to be made, a measured inductance and an ammeter, which was short-circuited when the break-flashes were produced. Except during the experiments with alternating current, the source of supply was a battery of dry cells.

These experiments were carried out during the years 1914 to 1916. I was assisted throughout by Mr. W. Mason, whilst the determinations of the duration of break-flashes with different metals were made by Mr. W. Shepherd, to both of whom I am greatly indebted.

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[*Received, November 3rd*, 1924.]

V.—*The Partial Formaldehyde Vapour Pressures of Aqueous Solutions of Formaldehyde. Part I.*

By ETHELBERT WILLIAM BLAIR and WILFRID LEDBURY.

A LARGE number of processes, based on methods of controlled oxidation of various hydrocarbons (Glock, D.R.-P. 109,014, 1898; Walters, F.P. 168,785; Willstätter and Bommer, *Annalen*, 1921, **422**, 36; Blair and Wheeler, *J. Soc. Chem. Ind.*, 1922, 304T; 1923, 81T; Berl and Fischer, *Z. angew. Chem.*, 1923, **36**, 297; Johnson, B.P. 199,885, 1922) have been proposed, from time to time, for the production, on a commercial scale, of aqueous solutions of formaldehyde. The comparatively low concentration of formaldehyde vapour in the effluent gases from such oxidation processes may easily result in depreciated yields of the required product, on account of low absorption efficiencies. It is the object of the present investigation to determine the partial formaldehyde vapour pressures of aqueous formaldehyde solutions of different strengths, and hence to ascertain whether, under equilibrium conditions of absorption, it is possible to effect, more or less completely, the fixation of highly diluted vapours of formaldehyde. Blair and Wheeler (*loc. cit.*) have shown that, under carefully regulated conditions, the slow oxidation of ethylene yields dilute formaldehyde vapours of concentration of the order of 1·0 to 2·0 mg. per litre, corresponding to vapour pressures of about 0·5 to 1·0 mm. of mercury respectively. The investigations carried out by the same authors, with the object of producing formaldehyde by the controlled oxida-

tion of methane, showed that formaldehyde vapours, ranging in concentration from 0·2 to 3·0 mg. per litre, corresponding to partial pressures of 0·13 to 1·65 mm. of mercury, were obtainable under the conditions of their laboratory experiments. In this connexion, it is of importance to determine the maximum strengths of aqueous formaldehyde solutions which are obtainable by the continuous absorption of such vapours under specified conditions. By a study of the partial formaldehyde vapour tensions of solutions at 0°, and by a comparison of the values so obtained with the corresponding values for 20°, the merits or demerits of low-temperature condensation, from the point of view of formaldehyde fixation, can be established. Further, the data derived at the lower temperature should indicate the feasibility, or otherwise, of obtaining formalin solutions of moderate strengths, by processes of chilling moist air or other gas containing small concentrations of the vapour.

Experimental.

Treatment of Formalin Solutions.—Samples of formalin, of approximately 40% strength by volume, and obtained from various sources, were found on analysis to contain varying amounts of methyl alcohol as impurity. The formaldehyde present was estimated by the hypoiodite method of Romijn (*Analyst*, 1897, **22**, 221; see also *Chem. Ztg.*, 1901, **25**, 740; *Ber.*, 1898, **31**, 1979; 1901, **34**, 2817), which, for sufficiently diluted solutions, provides trustworthy data, even when methyl alcohol is present (Bergstrom, *J. Amer. Chem. Soc.*, 1923, **45**, 2150). From a determination of the total carbon content in a given weight of formalin (Blank and Finkenbeiner, *Ber.*, 1906, **39**, 1326), it was possible to arrive at the quantity of methyl alcohol present in the solution. In particular cases, methyl alcohol was present to the extent of 5·0 to 10·0% by weight. It has been suggested by Ormandy and Craven in their "Note on Aqueous Formaldehyde Solutions," read before the Chemical Society, that the discrepancies in the previously published values for the densities of such solutions arise from the presence of methyl alcohol, and their results appear to substantiate this contention. In studying the physical properties of aqueous formaldehyde solutions, it is therefore imperative that any contaminating methyl alcohol should be eliminated. These workers succeeded in removing methyl alcohol from formalin solutions by prolonged refluxing with water; they showed that both the refractive index and the density of a purified formalin solution are linear functions of its concentration. Their data are in agreement with those obtained as a result of a similar investigation by Auerbach and Barschall, who, however, prepared aqueous solutions by passing nitrogen over heated paraformaldehyde

and absorbing in distilled water the formaldehyde vapour carried forward. The removal of methyl alcohol was effected, in the present instance, by refluxing the solutions with distilled water, the proportion of the latter being determined by the strength of the formaldehyde solution required. For this purpose was employed a litre flask, to which was attached a tube, 1 inch in diameter and 28 inches in length, packed to within a few inches of the top with glass beads. The heating was regulated so that the temperature registered at the head of the column was approximately the boiling point of methyl alcohol (66°). Refluxing for a period of about 36 hours sufficed to remove methyl alcohol from 500 c.c. of the solution; the odour of the alcohol, however, could not be detected when the refluxing had proceeded for only a few hours. Acetone was absent from the solution after refluxing. Incidentally, it is of interest in this connexion to note that the above method for the removal of methyl alcohol forms the basis of a recent patent for obtaining formalin with only a low content of methyl alcohol (Hirchberg, B.P. 199,759, 1922). The elimination of methyl alcohol from formaldehyde solutions, having concentrations of approximately 40% by volume, had a marked effect on the stability of these solutions, the tendency for paraformaldehyde to separate being enhanced by the removal of the alcohol. Thus a solution containing 5% of methyl alcohol and having a formaldehyde content of 41·0 g. per 100 c.c. did not deposit paraformaldehyde on prolonged exposure at 0°, whilst with an uncontaminated solution, containing 38·7 g. of formaldehyde per 100 c.c., a similar exposure caused the development of an opalescence within a few hours, and the eventual deposition of the solid white polymeride. This observation is not, however, in agreement with a surmise put forward by Hirchberg (*loc. cit.*), to the effect that methyl alcohol promotes the production of acetals such as methylal, which are stated to be conducive to the polymerisation of formaldehyde. In consequence of the separation of paraformaldehyde at 0° from the more concentrated formaldehyde solutions freed from methyl alcohol, it was not possible to determine the partial formaldehyde vapour pressures at 0° of solutions having strengths appreciably greater than 30%.

Subsequent to analysis, the formaldehyde solutions, obtained as a result of the above treatment, were allowed to stand at 15° over a prolonged period before being used for the vapour pressure measurements at 20° or 0°. To ascertain the effect of the presence of small amounts of methyl alcohol on the partial formaldehyde vapour pressures of the solutions, the pure alcohol was added to a series of the latter in such amounts as to provide in each case a constant ratio, CH_4O/CH_2O.

Method of Determination.—On account of the comparatively low vapour pressures involved at the ordinary temperature and more especially at 0°, even in the case of solutions approaching the strength of 40% by volume, the "dynamic" or "flow" method was employed in these determinations. Each "carburettor" was charged with 75 c.c. of the formaldehyde solution under investigation, this, in the case of a 40% formaldehyde solution, corresponding to the presence of 30,000 mg. of formaldehyde. At 20°, the passage of 100 litres of moist air through this solution, at the rate of 1·0 litre in 30 mins., effected the removal of only about 250 mg. of formaldehyde, so that for the purpose of computing formaldehyde vapour pressures the concentrations of the formalin solutions were assumed to remain constant during a run involving, say, the passage of 5, 10, 20, or 40 litres of moist air. At 0°, it was possible to pass through the solution much larger volumes of moist air without appreciably affecting the concentration. The estimation of the formaldehyde, carried over by the air stream into the absorption worms, was made by using the hypoiodite method of Romijn (*loc. cit.*), and from the data thus obtained the partial vapour pressure of the formaldehyde was calculated by use of the formula of Foote and Scholes (*J. Amer. Chem. Soc.*, 1911, **33**, 1309):

$$P = 760v_2/(v_1 + v_2) \text{ mm. of Hg,}$$

where $v_2 = 22{\cdot}4\ W/M$ litres, is the volume occupied by the formaldehyde vapour alone and M its molecular weight, whilst v_1, the volume of the air used, reduced to *N.T.P.*, is given by the expression

$$v_1 = 273Vp/760(273 + t).$$

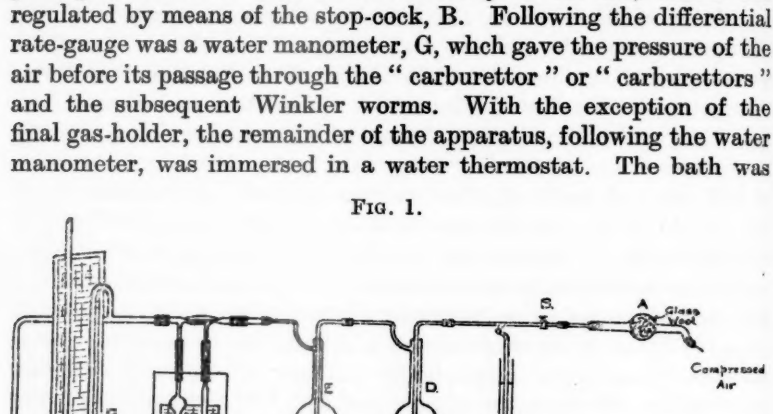
V is the unreduced volume of the air, p the pressure of the air collected in the final gas-holder, after necessary corrections have been made for water-vapour tension, and t is the temperature of the air collected in the gas-holder. An account of the applications and limitations of the "dynamic" method of determining vapour pressures is given by Thomas and Ramsay (J., 1923, **123**, 3257), who cite the views of Perman (*Proc. Roy. Soc.*, 1904, **72**, 72; *J. Physical Chem.*, 1905, **9**, 96), the latter, after a careful investigation of the subject, having concluded that, provided proper precautions are taken, the method is capable of yielding sufficiently accurate results.

Apparatus.

The accompanying diagram (Fig. 1) shows the details of the apparatus employed in this investigation. A controlled supply of compressed air was passed through a dust-filter, A, consisting of an enclosed plug of glass wool, and after travelling beyond the stop-cock B, and the pressure regulator, C, was bubbled successively through potash solution and distilled water in D and E, respectively.

A calibrated differential rate-gauge, constructed on the Venturi principle, served to indicate the velocity of the air, which was regulated by means of the stop-cock, B. Following the differential rate-gauge was a water manometer, G, whch gave the pressure of the air before its passage through the " carburettor " or " carburettors " and the subsequent Winkler worms. With the exception of the final gas-holder, the remainder of the apparatus, following the water manometer, was immersed in a water thermostat. The bath was

FIG. 1.



inserted in a large wooden box, and the intervening space between the bath and the walls of the box was loosely packed with lagging, consisting of a mixture of magnesite and asbestos fibre. For the experiments at 20°, the requisite temperature was maintained (within $\pm$ 0·05°) by means of a Lowry thermo-regulator, whilst ice uncontaminated with foreign substances was introduced into the bath to keep the temperature at 0°. The long worm, H, served to bring the inflowing air to the required temperature. This was followed by a specially designed " carburettor " (or, in the experiments at 0°, by two " carburettors ") containing 75 c.c. of the formaldehyde solution under investigation. The object of its

construction was to permit the incoming stream of air to pass through the formaldehyde solution in the vertical worm, and to cause the air bubbles, as they emerged into the splash-trap at the top, to force over a part of the formaldehyde solution at the head of the worm into the glass reservoir shown. Fresh formaldehyde solution was thus drawn in at the base of the vertical worm and the unsaturated air came at the outset into contact with fresh formalin solution. At 20°, when two such " carburettors " were connected in series, the amount of formaldehyde vapour carried over by a given volume of air was practically unchanged; hence, at 20°, one " carburettor " only was in use during the greater part of the investigation. The air, saturated at this stage with formaldehyde vapour, passed along the horizontal tube, L, which, in the experiments at the higher temperature, was maintained above the temperature of the bath by an electrically heated coil of resistance wire. Under these conditions, no condensation of water vapour and consequent premature absorption of formaldehyde vapour occurred during the passage of the vapour-laden air along the tube. For the absorption of formaldehyde vapour, two or three Winkler worms containing distilled water were connected in series. The issuing air, stripped of formaldehyde vapour, entered a graduated, water-filled gas-holder at a pressure which was maintained constant, throughout the whole of the experiments, by means of a constant-level overflow. By employing a constant height of formaldehyde solution in the " carburettor " and constant heights of water in the Winkler worms, and by making the necessary alterations in the level of the overflow, the pressure of the air entering the " carburettor," and issuing therefrom, was kept constant. Thus the pressure conditions throughout the whole series of determinations were standardised. Such an adjustment of pressure conditions is necessary, since the amount of formaldehyde carried over by a given reduced volume of air is dependent on the pressure of its delivery as well as on the temperature. The air was forced through the apparatus at a velocity of 1 litre in 30 mins., since it was found from preliminary trials that if the rate of flow was diminished below this value, the amount of formaldehyde vapour per unit volume of air was unaltered for a given formalin solution. Adopting the method of procedure outlined above, a number of determinations were made of the partial formaldehyde vapour pressure of each solution under investigation. For each determination, totals of 5, 10, 15, or 20 litres of moist air were passed, according to the strength of the formalin solution in the " carburettor."

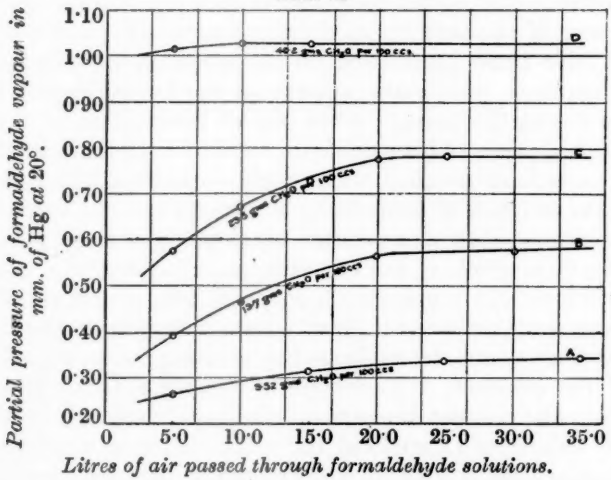
As a result of data derived from earlier experiments, it was found justifiable to dispense with the third Winkler worm of the absorption

train, since even in the case of the relatively concentrated vapours, issuing from a solution containing 38 g. of formaldehyde per 100 c.c., there was no detectable amount of formaldehyde in the water at this stage. In the case of the second absorption worm, small amounts of formaldehyde of the order of 0·1 to 0·2 mg. were found condensed during the passage of the more concentrated vapours. This worm was permanently retained throughout the investigation.

Formaldehyde Vapour Pressures of Aqueous Formaldehyde Solutions at 20°.

Formalin solutions, from which methyl alcohol had been eliminated in the manner previously described, were exposed at 15° before

FIG. 2.



introduction into the "carburettor." The "carburettor" and its contents were then left over-night in the thermostat at 20°, prior to the vapour-pressure determinations.

With the exception of the formaldehyde solution of approximately 40% strength, all the solutions examined exhibited exceptionally low initial formaldehyde vapour pressures, but, as increasing volumes of air, for successive determinations, were passed through each of these solutions, the pressure values increased, rapidly at first, then more slowly, rising to constant maximum values.

The accompanying curves, A, B, C, and D (Fig. 2) depict graphically the relationship between the partial pressure of the formaldehyde vapour in mm. of mercury and the total volume of air in litres passed through a solution of given strength. The examination of the formalin solution containing 40·2 g. of formal-

dehyde per 100 c.c. did not reveal, on the part of the partial pressure, any marked tendency to increase in magnitude, such as was evidenced with the more dilute solutions.

The equilibrium or asymptotic values of the formaldehyde vapour pressures, that is, the constant values reached when the passage of a sufficient volume of air through the solutions had brought about apparent equilibrium conditions between the liquid and vapour phases, are given in Table I, together with the corresponding concentrations of formaldehyde vapour in the effluent air.

TABLE I.

Gms. of formaldehyde per 100 c.c. of formalin solution	9·52	19·7	29·5	31·1	40·2
Mg. of formaldehyde vapour per litre of issuing air	0·59	1·01	1·39	1·40	1·75
Partial pressure of formaldehyde vapour in mm. of mercury	0·340	0·575	0·780	0·795	1·025

FIG. 3.

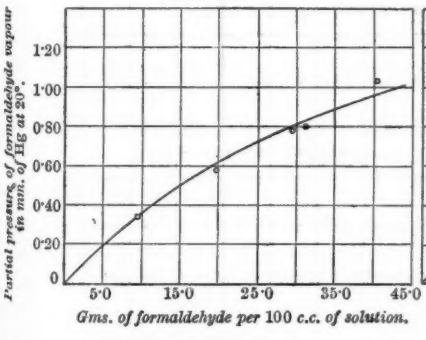
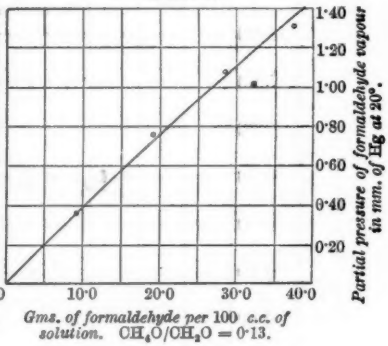


FIG. 5.



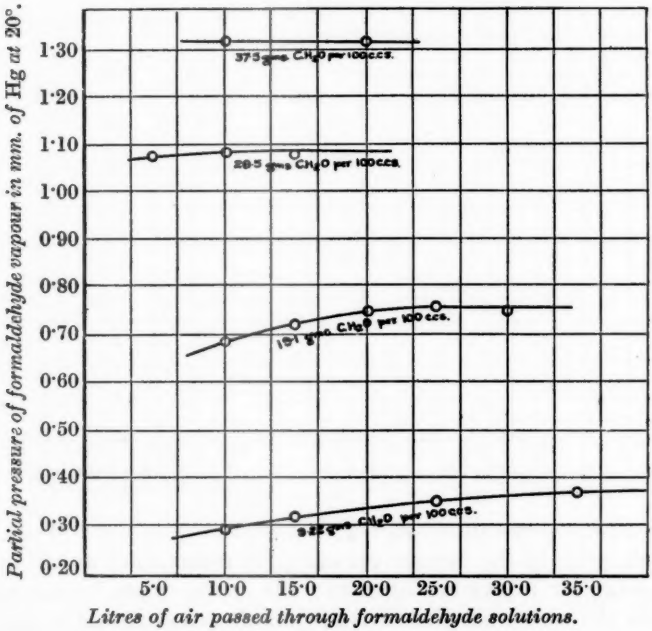
The solution containing 31·1 g. of formaldehyde per 100 c.c. was exposed, prior to the vapour-pressure determinations, at 20° in the thermostat for a number of days; the value given in the above table for the vapour pressure is the mean of several almost coincident values, *viz.*, 0·797, 0·793, 0·795 mm. of Hg, which were subsequently obtained.

In Fig. 3, the partial pressures of the formaldehyde vapour, expressed in mm. of mercury, are plotted as ordinates against the corresponding concentrations of the aqueous formaldehyde solutions in g. per 100 c.c. as abscissæ. It is seen that the partial pressure of the formaldehyde vapour is not a linear function of the formaldehyde concentration in the liquid phase (compare the relation between density and refractive index of a formaldehyde solution and the concentration of the latter as demonstrated by Ormandy and Craven, *loc. cit.*), but that the rate of increase of the partial pressure

with the concentration falls off slightly with increasing concentration of the solution.

Addition of Methyl Alcohol to Aqueous Formaldehyde Solutions at 20°.—Pure methyl alcohol, free from acetone, was added to the aqueous formaldehyde solutions treated in the manner previously described, in such amount that for all the solutions a constant small ratio CH_4O/CH_2O, *viz.*, 0·13 by weight, was preserved. As in the case of the purified aqueous formaldehyde solutions, there was again, for certain solutions, a rise in the vapour pressure values until maximum values were attained.

FIG. 4.



A comparison of the curves in Fig. 2 with those in Fig. 4 shows the effects of addition of small quantities of methyl alcohol to aqueous formaldehyde solutions. The partial pressure values at the outset approximate more closely to the final maximum values than is the case with uncontaminated formaldehyde solutions; the apparent equilibrium vapour pressures are raised in all cases above those previously determined; and the difference of vapour pressure due to increase in the formaldehyde concentration of the solution is more pronounced in this series of determinations. Table II gives the apparent equilibrium values of the partial pressures of these formalin solutions, together with the corresponding concen-

trations of formaldehyde vapour in the effluent air. The curve (Fig. 5) shows diagrammatically the relation of the partial pressure of the formaldehyde vapour to the formaldehyde concentration of the solution.

TABLE II.

Gms. of formaldehyde per 100 c.c. of formalin solution. CH_4O/CH_2O = 0·13	9·22	19·1	28·5	37·5
Mg. of formaldehyde vapour per litre of issuing air	0·62	1·29	1·86	2·32
Partial pressure of formaldehyde vapour in mm. of Hg	0·362	0·760	1·08	1·31

When the formaldehyde-content of the solution is expressed in g. per 100 c.c., there is a nearer approach in this case to a straight line relationship between formaldehyde-concentration and the corresponding partial pressure of formaldehyde vapour. There is a still nearer approach to a linear relationship when the formaldehyde-concentration is expressed as g. per 100 g. of solution, since the specific gravities of formalin solutions increase with concentration, the value for a 40% solution being about 1·08.

Formaldehyde Vapour Pressures of Aqueous Formaldehyde Solutions at 0°.

Formalin solutions, freed from methyl alcohol, were allowed to stand at the ordinary temperature for several days and subsequently introduced into the " carburettors " (two in series were employed in these experiments at 0°). Prior to the vapour-pressure determinations, the " carburettors " were left in the thermostat over-night at 0°.

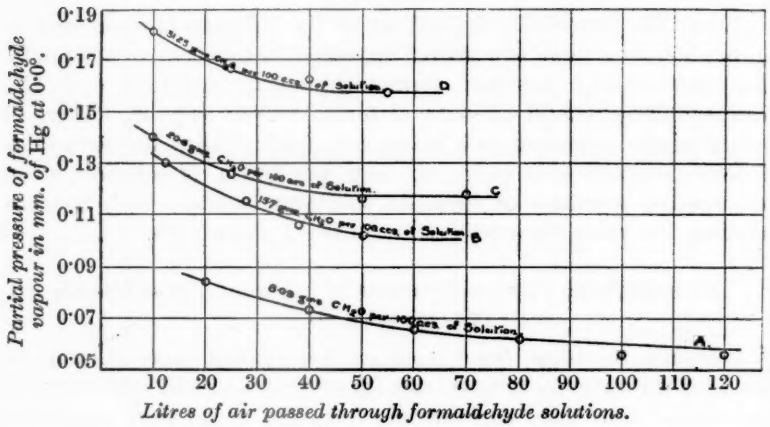
With each of the solutions examined, as increasing volumes of air were passed, the partial vapour pressures *decreased*, fairly rapidly at first, and then more slowly reached an almost constant *minimum* value. It will be remembered that the partial vapour pressure rose to an approximately constant maximum value when a purified formalin solution, after standing for a short period at 15°, was introduced into a thermostat at 20°, and air passed for the purpose of determining its partial formaldehyde vapour pressure at that temperature.

The accompanying curves, A, B, C, and D of Fig. 6, show graphically the manner in which the partial formaldehyde vapour pressures of the solutions decrease as increasing volumes of air are passed.

The apparent equilibrium values of the formaldehyde vapour pressures, that is, the constant minimum values reached when the passage of a sufficient volume of air through the solutions has

brought about apparent equilibrium conditions between liquid and vapour phases, are given in Table III, together with the corresponding concentrations of formaldehyde vapour in the effluent air. In the case of a formaldehyde solution, containing 16 g. of formaldehyde per 100 c.c., which had been exposed at 0° in the thermostat for 12 days before the passage of air, partial pressure values were obtained which were constant from the commencement; *viz.*, 0·104, 0·100, 0·102 mm. of Hg. The mean of these values falls very closely to the curve in Fig. 7.

FIG. 6.



Litres of air passed through formaldehyde solutions.

TABLE III.

Gms. of formaldehyde per 100 c.c. of formalin solution	8·09	15·68	20·63	31·25
Mg. of formaldehyde vapour per litre of issuing air	0·095	0·166	0·201	0·265
Partial pressure of formaldehyde vapour in mm. of Hg	0·056	0·102	0·118	0·157

From the data provided in Table III and from the curve of Fig. 7, it is evident that the partial formaldehyde vapour pressure is not a linear function of the concentration of the solution, but that increase in partial pressure with concentration is less pronounced at 0°. For the purpose of comparing the partial formaldehyde vapour-pressure values at 0° with those previously determined at 20°, the curves A and B are given in Fig. 8. A is the partial formaldehyde vapour-pressure–solution-concentration curve for 0°, and B the corresponding curve, plotted on the same scale, for 20°. For reasons cited above, it was not possible to study the vapour-pressure characteristics of formalin solutions much above 30% in strength.

The ratio Pressure of formaldehyde vapour at 0°/Pressure of

formaldehyde vapour at 20° varies progressively from 0·18 for a solution containing 30 g. of formaldehyde per 100 c.c. to 0·22 for a solution containing 5 g. of formaldehyde per 100 c.c., whilst the ratio Pressure of aqueous vapour at 0°/Pressure of aqueous vapour at 20° = 4·53/17·4 = 0·26.

From these values, it appears it is possible to obtain a more concentrated formalin solution by chilling warm air or gas, containing water vapour and formaldehyde vapour, to 0°, than by cooling the same gas to 20°. In such a process, the difference of solution strength at the two temperatures would be more pronounced in the case of the more concentrated vapours.

FIG. 7.

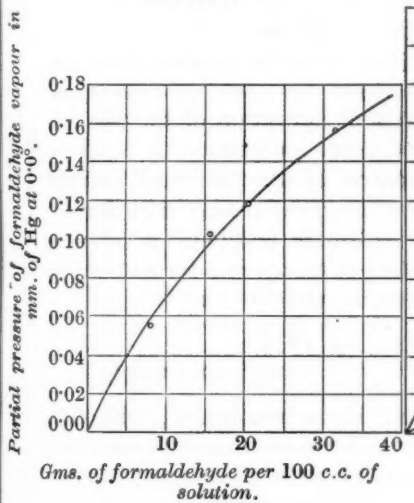
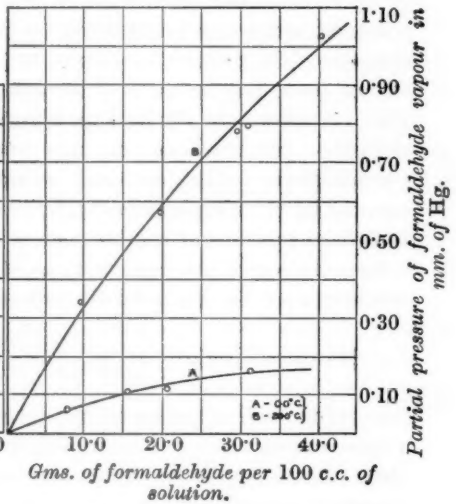


FIG. 8.



Addition of Methyl Alcohol to Aqueous Formaldehyde Solutions at 0°.—To aqueous formaldehyde solutions, methyl alcohol, free from acetone, was added in such amount that the ratio $WtCH_4O/WtCH_2O$ =0·13, this being the ratio employed in the corresponding vapour-pressure determinations at 20°. The data obtained for the solutions studied indicated that the addition of small amounts of methyl alcohol to aqueous formaldehyde solutions had very little effect on the final formaldehyde partial vapour pressure values of such solutions.

Thus from the curve (Fig. 7) it is seen that the vapour pressure of an aqueous solution containing 10·8 g. of formaldehyde per 100 c.c. in the absence of methyl alcohol is very approximately equivalent to 0·07 mm. of mercury. This value is almost identical with that obtained with a solution of corresponding strength containing a little

methyl alcohol ($CH_4O/CH_2O = 0{\cdot}13$ by weight), *viz.*, 0·072 mm. of mercury. The divergence between the initial and final values is not so pronounced as in the previous instance.

Discussion of Results.

Aqueous formaldehyde solutions do not exhibit the characteristic properties of gas–water systems, but on the contrary, at the ordinary temperature, behave, from the point of view of partial vapour pressures, in a manner suggestive of solutions in water of a soluble liquid of comparatively high boiling point, *e.g.*, glycerol in water. Determinations of the apparent molecular weight of formaldehyde in its aqueous solutions, as well as the vapour tension characteristics of these solutions, indicate the existence in the dissolved state of complex molecules in addition to the simple molecules of formaldehyde. The heavier molecules of the solute may include, not only one or more polymerides of formaldehyde, but also products, complex or otherwise, derived as a result of hydration of the formaldehyde; consideration of the distinctive properties of aqueous formaldehyde solutions and evidences of the residual affinity exerted by the simple formaldehyde molecule by reason of its doubly linked oxygen atom render such a postulate feasible. A possible interpretation of the conditions existing in an aqueous formaldehyde solution may be symbolically represented as follows :—

$$\text{[Formaldehyde]} \begin{matrix} \text{complex,} & \longrightarrow & CH_2O \\ \text{hydrated, etc.} & \longleftarrow & \text{(simple molecules).} \end{matrix}$$

Assuming the representation provides a reasonable, although vague, conception of the equilibrium conditions within the solution, then from apparent molecular-weight determinations, vapour-pressure considerations, etc., the equilibrium at the ordinary temperature must correspond to a large excess of the heavier molecules. The partial pressure, at a particular temperature, of the formaldehyde vapour above an aqueous formaldehyde solution will be almost entirely dependent on the concentration of the simple molecular form of the aldehyde, since the heavier molecules will possess a low volatility in view of their relatively high molecular weights.

When a formaldehyde solution which had been treated for the removal of methyl alcohol was introduced into a thermostat maintained at 20°, after previously standing for several days at 15°, and air was bubbled through the solution as in the above determinations, there was an increase of the formaldehyde vapour pressure to a constant maximum value as increasing volumes of air were passed. Air passing through the solution at any particular moment takes up

formaldehyde vapour in amount corresponding to the concentration of simple formaldehyde molecules. It is assumed that the *new* equilibrium conditions between the complex and the simple molecules in solution, brought about by raising the temperature, is only gradually approached as time elapses, but that the velocity of this approach, or, in other words, the amount of simple formaldehyde produced in unit time at 20° by the transformation of the complex, is greater than the rate of removal of formaldehyde from solution under the influence of its vapour pressure; this vapour pressure being a function of the concentration of the simple molecular form of the aldehyde. Since the velocity of transformation is initially greater than that of removal, simple formaldehyde will accumulate at this temperature in excess of its original concentration. This accumulation of the simple form will exert a two-fold influence; first, by reason of its active mass in solution, it will lower the velocity of transformation of the complex, and, secondly, it will increase the velocity of the removal of formaldehyde from solution, since the latter is dependent on the concentration of the simple molecular form. In the course of time the two velocities will be equalised and the amount of formaldehyde vapour removed at 20°, by the passage of air from the solution in a given time, will reach a constant maximum value.

The gradual attainment of constant values by the formaldehyde vapour pressures at 0° can also be explained by the gradual readjustment of the equilibrium conditions between complex and simple molecules in solution, necessitated by change of temperature. A formaldehyde solution which had been exposed for several days at 20°, prior to determinations at 20° being carried out, provided a series of vapour pressure values which were almost constant from the outset. These values corresponded with a point lying very close to the curve of Fig. 3. A similar procedure in the case of a solution at 0° made it evident that in this case also the equilibrium condition had been brought about by prolonged exposure at the temperature under consideration. The latter observations lend support to the hypothesis put forward in explanation of the variations involved.

The addition of a small amount ($CH_4O/CH_2O = 0{\cdot}13$) of methyl alcohol to an aqueous formaldehyde solution not only brings about, at 20°, a nearer approach of the vapour pressure determined at the outset to those determined after the passage of large volumes of air, but also produces a considerable increase (0·60 to 0·80 mm. of Hg for a solution containing 20 g. of CH_2O per 100 c.c.) in the constant maximum values eventually attained. At 0°, the equilibrium vapour pressure values were affected only very slightly by the addition of small amounts of methyl alcohol. In the course of a

further investigation, the results of which it is hoped to publish at a later date, it was found that the partial formaldehyde vapour pressure of a 15% methyl-alcoholic solution of formaldehyde at 20° was more than double that of an aqueous solution of corresponding strength. This would explain the relatively high values found for the formaldehyde vapour pressures of formalin solutions containing methyl alcohol, including solutions of commercial formalin.

Summary.

The partial formaldehyde vapour pressures of aqueous formaldehyde solutions, freed from methyl alcohol, have been determined at 20° and 0° by the "dynamic" method.

After an initial exposure of a solution at 15°, an increase of the partial pressure values, as increasing volumes of air were passed until the subsequent attainment of a constant *maximum* value, was noted at 20°, whilst at 0° the continuous passage of air through a solution was shown to bring about a lowering of the partial formaldehyde vapour pressure until a constant *minimum* value was reached.

The addition of methyl alcohol to an aqueous formaldehyde solution decreases the divergence between the initially and finally observed values of the partial formaldehyde vapour pressures, and, in the case of solutions at 20°, enhances the constant maximum value eventually obtained. Under these latter conditions, there is a nearer approach to a linear relationship between formaldehyde partial vapour pressure and concentration.

An hypothesis has been put forward to explain certain of the observations made.

Further investigations are being made on the properties of aqueous and methyl-alcoholic solutions of formaldehyde.

This work was carried out for the Chemistry Research Board of the Department of Scientific and Industrial Research, to whom we are indebted for permission to publish these results.

MAIN LABORATORY, R.N. CORDITE FACTORY,
HOLTON HEATH, DORSET. [*Received, September 9th*, 1924.]

VI.—*The Detection of Methylamine in Presence of Excess of Ammonia.*

By P. A. VALTON.

A CONVENIENT method for the differentiation of methylamine and ammonia depends on the much greater reactivity of the former with 2 : 4-dinitrochlorobenzene; the product, 2 : 4-dinitromethyl-

aniline, is very sparingly soluble in alcohol, readily crystallised, and easily identifiable, melts sharply at 175·5°, and depresses the m. p. of 2 : 4-dinitroaniline (179°). The method can be used for detecting small quantities of methylamine in presence of excess of ammonia.

When a dilute alcoholic solution of dinitrochlorobenzene is treated with ammonia at the ordinary temperature, no dinitroaniline separates after 20 hours, although the solution slowly becomes yellow; on the other hand, with methylamine the yellow colour develops rapidly and after 18 to 20 hours dinitromethylaniline crystallises out. The smallest quantities of methylamine hydrochloride which could be identified by this means were 0·005 g. when alone, and 0·008 g., 0·01 g., and 0·02 g. in presence of 0·08 g., 1 g., and 20 g., respectively, of ammonium chloride. Dimethylamine interferes, but the method is still applicable if the amount of dimethylamine does not exceed 10% of the methylamine. The minimum quantity of methylamine hydrochloride which could be identified was 0·02 g. in presence of 0·2 g. of ammonium chloride and 0·002 g. of dimethylamine hydrochloride, and 0·04 g. in presence of 4 g. of ammonium chloride and 0·004 g. of dimethylamine hydrochloride.

The method employed was as follows. The solution containing the methylamine and ammonium salts was introduced into a 250 c.c. flask with a Kjeldahl splash-trap, and 30 c.c. of 2*N*-sodium hydroxide were added together with enough water to bring the volume up to 80 c.c. The mixture was distilled into 10 c.c. of a 0·5% alcoholic solution of 2 : 4-dinitrochlorobenzene in a graduated tube, the adapter of the condenser dipping nearly to the bottom. When the volume of the solution had reached 20 c.c., the distillation was stopped and the solution left for 20 hours. The precipitated dinitromethylaniline was crystallised once from alcohol and identified by the method of mixed melting points. When the minimum amount of methylamine was used, the amount of precipitate was sometimes too small for crystallisation, but the crude product, after being washed with a little alcohol, melted above 170° and, on admixture with dinitromethylaniline, between 170° and 175°. When there was but 0·02 g. of methylamine hydrochloride mixed with 20 g. of ammonium chloride, the former was concentrated by evaporating the solution to dryness, extracting the dry salt with 50 c.c. of hot alcohol, and using this extract in the distillation.

UNIVERSITY COLLEGE, LONDON. [*Received, July 10th*, 1924.]

VII.—*Nitro-derivatives of* o-*Cresol.*

By GEORGE PHILIP GIBSON.

THE direct nitration of *o*-cresol has been studied by many chemists; the chief products are 3-nitro-*o*-cresol and 5-nitro-*o*-cresol, although Spiegel, Munblit, and Kaufmann (*Ber.*, 1906, **39**, 3240) record the formation of a little 3 : 5-dinitro-*o*-cresol (compare Hofmann and Millar, *Ber.*, 1881, **14**, 568; Rapp, *Annalen*, 1884, **224**, 175; Schultz, *Ber.*, 1907, **40**, 4319; Wieland, Bernheim, and Böhm, *Ber.*, 1921, **54**, 1776); all workers have given the melting point 70° for 3-nitro-*o*-cresol, but the recorded melting point of 5-nitro-*o*-cresol ranges from 79° to 95°.

The author has attempted to elucidate these discordant results, although his main object has been the investigation of certain derivatives of 3-nitro-*o*-cresol, which were required for another research.

The greater part of the material used was prepared by Hofmann and Millar's method, although Schultz's procedure proved to be the best for mononitration owing to the ease with which the temperature and concentration can be regulated. Using the first method, if 3- and 5-nitro-*o*-cresols are the desired products, the conditions of nitration must be carefully adhered to, otherwise 3 : 5-dinitro-*o*-cresol may be the main product of the reaction.

The fact that pure 5-nitro-*o*-cresol is dimorphous and the presence of 3 : 5-dinitro-*o*-cresol and of tarry materials in the residue after the removal of the 3-nitro-*o*-cresol render the isolation of 5-nitro-*o*-cresol somewhat troublesome; although these difficulties have been overcome, the yield is poor.

5-Nitro-*o*-cresol forms a monohydrate melting at 30—40° (Neville and Winther, *Ber.*, 1882, **15**, 2978), which possesses properties very different from those of otherwise similar nitrocresols, which are anhydrous; crystallisation from aqueous solvents is therefore an excellent method for removing 3 : 5-dinitro-*o*-cresol from 5-nitro-*o*-cresol. Anhydrous 5-nitro-*o*-cresol crystallises in two forms which are interconvertible. One, the pale yellow, unstable form, which separates first, passes when it is left in the presence of solvents, crushed or rubbed, into the more stable, colourless variety.

Previous workers have usually obtained derivatives of the above-named nitro-*o*-cresols by the nitration of the tolyl ethers and esters (Hofmann and Millar, *loc. cit.*; Borsche, *Ber.*, 1923, **56**, 1488; Stadel, *Annalen*, 1883, **217**, 155; Reverdin, *Ber.*, 1902, **35**, 1444; 1912, **45**, 1450). In all cases, the orientation of the nitro-group is not certain and the structures of a number of these derivatives have

therefore been established by preparing the compounds directly from pure 3- and 5-nitro-*o*-cresols, and from 3 : 5-dinitro-*o*-cresol (compare Ullmann and Sané, *Ber.*, 1911, **44**, 3730; Cain and Simonsen, J., 1914, **105**, 156; Spiegel, Munblit, and Kaufmann, *loc. cit.*; Hofmann and Millar, *loc. cit.*).

In the case of derivatives of 5-nitro-*o*-cresol, ordinary methods give excellent yields, but with 3-nitro- and 3 : 5-dinitro-*o*-cresol, probably owing to the presence of two groups ortho to the reacting hydroxyl group, poor results are obtained even when the temperature is raised and the time prolonged.

For the preparation of derivatives other than the acetates (Smith and Orton, J., 1908, **93**, 1250), the dry sodium salts of 3-nitro- and 3 : 5-dinitro-*o*-cresol were heated at high temperatures with benzoyl chloride, toluene-*p*-sulphonyl chloride, methyl sulphate, and methyl toluene-*p*-sulphonate, respectively (compare Hofmann and Millar, *loc. cit.*; Cain and Simonsen, J., 1914, **105**, 156). The yields were satisfactory and the reactions took place in two directions, the proportions of the products depending on the nature of the reagent.

In the case of benzoyl chloride and toluene-*p*-sulphonyl chloride, the products were chiefly the corresponding benzoates and toluene-*p*-sulphonates with very small proportions of the corresponding chloronitrotoluene or chlorodinitrotoluene (compare Ullmann and Sané, *loc. cit.*).

In the experiments with methyl sulphate and sodium 3-nitro-*o*-tolyl oxide, the purity of the reagent seems to be the determining factor. Using pure methyl sulphate, the yield of the methyl ether is nearly theoretical, but if methyl hydrogen sulphate is present very serious complications arise and the yield may fall below 50%; sulphonic derivatives of 3-nitro-*o*-cresol and its methyl ether are produced with appreciable charring, the small amount of impurity (10% in commercial methyl sulphate) acting as an intermediary according to the equation

$$R{\cdot}H + OH{\cdot}SO_2{\cdot}OMe \longrightarrow R{\cdot}SO_2{\cdot}OMe + H_2O,$$

where R is $NO_2{\cdot}C_6H_2Me{\cdot}OH$ (I) or $NO_2{\cdot}C_6H_2Me{\cdot}OMe$ (II) (compare C. S. Gibson and Vining, J., 1923, **123**, 840; Simon and Frèrejacque, *Compt. rend.*, 1923, **176**, 900).

In the case of 3 : 5-dinitro-*o*-cresol, methylation takes place quantitatively in either of the above cases, because the 5-position is occupied, so that sulphonic derivatives cannot readily be formed; using methyl or ethyl toluene-*p*-sulphonate with the above dry sodium salts, good yields of the corresponding ethers are easily obtained.

EXPERIMENTAL.

Preparation of 3- *and* 5-*Nitro*-o-*cresols*.—A mixture of nitric acid (107 c.c.; *d* 1·42) and glacial acetic acid (300 c.c.) was stirred in a freezing mixture at — 15° while a mixture of *o*-cresol (100 g.) and glacial acetic acid (100 c.c.) was added in the course of 2 hours, when a thick magma of crystals separated. After standing 2 hours in the freezing mixture, the mass was poured into water (5000 c.c.), the crystals were separated, and submitted to steam distillation, when crude 3-nitro-*o*-cresol (yield 35%) containing a small proportion of 3 : 5-dinitro-*o*-cresol passed over; 5-nitro-*o*-cresol mixed with a little (10%) 3 : 5-dinitro-*o*-cresol then remained in the flask as an oil, which solidified when cold.

The crude distillate, m. p. 55—65°, was fractionally distilled in steam, and the various fractions were crystallised from petroleum (b. p. 80—100°). The first fractions gave deposits of deep yellow plates of nearly pure 3-nitro-*o*-cresol; the last gave pure 3 : 5-dinitro-*o*-cresol in well-defined, colourless prisms. The 3-nitro-compound may also be isolated by the crystallisation of the crude sodium salt from water.

Pure 3 nitro-*o*-cresol has b. p. 102—103°/9 mm. and m. p. 70°.

The residue from the steam distillation was crystallised from a large quantity of 50% alcohol, when crude 3 : 5-dinitro-*o*-cresol was deposited, the 5-nitro-*o*-cresol remaining in solution. The filtered solution was evaporated and the dark oily residue purified by distillation (b. p. 186—190°/9 mm.), by distillation in superheated steam at 180°, or by crystallisation of the sodium salt from water; in the last two cases, the monohydrate was dried at 100° and the anhydrous compound crystallised from a dry solvent such as benzene.

Anhydrous 5-nitro-*o*-cresol is deposited from a hot benzene solution in fine, yellow needles which, when left in the mother-liquor for a day or two, redissolve and crystallise again in large, colourless plates; the change takes place slowly from one or two centres of crystallisation, so that the line of advance of the transformation is quite distinct throughout the process. On attempting to separate the needles by filtration, they immediately fall to powder when touched or pressed, and are transformed into the plates with the correct melting point. With great care, the needles may be isolated and they remain clear for a short time, but eventually become opaque. Similar phenomena to the above occur in other solutions with more or less rapidity, but are most characteristic in benzene.

Owing to the readiness with which the unstable form is converted into the stable, both seem to melt at 96°; if great care is taken to procure the needles unchanged, the melting point is sometimes as low as 75°, but it depends on the rapidity of the heating.

On crystallisation from aqueous alcohol or acetone, 5-nitro-*o*-cresol is deposited in very fine needles of the mono-hydrate, m. p. 30—40° as stated by Neville and Winther (*Ber.*, 1882, **15**, 2978).

Preparation of 3 : 5-*Dinitro*-o-*cresol.*—A mixture of nitric acid (150 c.c.; *d* 1·42) and glacial acetic acid (300 c.c.) was cooled in ice and mechanically stirred while a solution of *o*-cresol (100 g.) in glacial acetic acid (100 c.c.) was gradually added. After standing at the ordinary temperature for 24 hours, the product was poured into water, the granular solid separated, and distilled in steam to remove a small amount of crude 3-nitro-*o*-cresol (yield 10%). The residue in the flask was chiefly 3 : 5-dinitro-*o*-cresol with some 5-nitro-*o*-cresol (10%) and tarry materials. After crystallisation from 50% alcohol (p. 44), the dark brown 3 : 5-dinitro-*o*-cresol was converted into the sodium salt, when the colouring matter remained in the mother-liquor and the pure salt was obtained.

Pure 3 : 5-dinitro-*o*-cresol is slightly volatile in steam (3 g. per litre) and can be recrystallised from 50% aqueous alcohol or petroleum (b. p. 60—80°).

The Sodium Salts.—As the sodium salts of the nitro-*o*-cresols are fairly readily soluble in water and appear to hydrolyse during the process of drying at 100°, they are best prepared in the pure state by treating a suspension of sodium ethoxide in boiling benzene with a benzene solution of a slight excess of the nitro-compound; the products are separated and washed with dry benzene.

Sodium 3-*nitro*-o-*tolyl oxide* crystallises from water in deep red plates ($+ 2H_2O$); at 100°, it sinters and then gives the anhydrous compound as a light brick-red powder (Frazer, *Amer. Chem. J.*, 1903, **30**, 309). Sample prepared with sodium ethoxide (Found : Na = 13·10. Calc. for $C_7H_6O_3NNa$, Na = 13·14%).

Sodium 5-*nitro*-o-*tolyl oxide* crystallises from water in yellow, hydrated needles, which, at 100°, without sintering, give a beautiful cerise, anhydrous salt. Specimen prepared with sodium ethoxide (Found : Na = 13·15%).

Sodium 3 : 5-*dinitro*-o-*tolyl oxide* forms a deep yellow solution and crystallises in yellow, hydrated needles which, without softening at 100°, give a deep brick-red powder. Specimen dried at 100° (Found : Na = 10·5. $C_7H_5O_5N_2Na$ requires Na = 10·46%).

Pyridine 3 : 5-*dinitro*-o-*tolyl oxide*, $C_{12}H_{11}O_5N_3$, separates in orange needles when a solution of 3 : 5-dinitro-*o*-cresol (2 g). in a hot mixture of pyridine (2 g.) and benzene (10 c.c.) is cooled. It melts at 96° and gradually dissociates in the air and in solution, but it can be recrystallised from dry solvents containing a little pyridine (Found : C = 52·2; H = 4·1. $C_{12}H_{11}O_5N_3$ requires C = 52·0; H = 4·0%).

The Acetyl Derivatives.—*5-Nitro-o-tolyl acetate*, $NO_2 \cdot C_6H_3Me \cdot OAc$, was formed by the action of acetic anhydride on pure 5-nitro-*o*-cresol in dry pyridine at the ordinary temperature. After 12 hours, the solution was diluted with water, extracted with ether, and the extract shaken with dilute acid and then with dilute sodium hydroxide solution. The ether was evaporated and the solid residue crystallised from a mixture of petroleum (b. p. 80—100°) and acetone (large prisms) or from alcohol (needles).

This ester, m. p. 88°, is readily soluble in acetone, benzene, or chloroform, but sparingly soluble in alcohol, carbon tetrachloride, or light petroleum (Found: C = 55·3; H = 4·6. $C_9H_9O_4N$ requires C = 55·4; H = 4·6%).

3-Nitro-o-tolyl acetate was prepared by treating pure 3-nitro-*o*-cresol (5 g.) at the ordinary temperature with acetic anhydride (15 c.c.) containing a trace of concentrated sulphuric acid (Smith and Orton, *loc. cit.*) until the yellow colour of the nitrocresol had disappeared; water was added, the oily ester extracted with ether, the extract washed with dilute caustic soda and evaporated; the residue crystallised from alcohol in large tablets, m. p. 42°. This acetate is readily soluble in the ordinary organic solvents and crystallises well from alcohol or petroleum (b. p. 60—80°) (Found: C = 55·4; H = 4·5%).

3 : 5-Dinitro-o-tolyl acetate, $C_6H_2Me(NO_2)_2 \cdot OAc$, prepared in a similar manner, melts at 96° and crystallises readily from alcohol. It is fairly soluble in alcohol, acetone, benzene, or chloroform, but sparingly soluble in petroleum (b. p. 60—80°) or carbon tetrachloride (Found: C = 44·8; H = 3·4. $C_9H_8O_6N_2$ requires C = 45·0; H = 3·3%).

The Benzoyl Derivatives.—*5-Nitro-o-tolyl benzoate*,

$$NO_2 \cdot C_6H_3Me \cdot OBz,$$

was prepared in the same way as the corresponding acetate (above), a slight excess of pure benzoyl chloride being used in place of acetic anhydride.

It melts at 128°, is sparingly soluble in ether, alcohol, or light petroleum and fairly soluble in acetone, benzene, chloroform, or carbon tetrachloride (Found: C = 65·3; H = 4·3. $C_{14}H_{11}O_4N$ requires C = 65·4; H = 4·28%).

3-Nitro-o-tolyl benzoate was obtained by heating anhydrous sodium 3-nitro-*o*-tolyl oxide (p. 45) with pure benzoyl chloride (2 mols.) for 1 hour at 120°. The product was treated in the cold with a mixture of pyridine, water, and ether; the ethereal solution was shaken successively with acid and with dilute alkali and finally evaporated; the residue crystallised from alcohol or petroleum (b. p. 60—80°) in needles, m. p. 42°, b. p. 218—220°/9 mm. This

ester is soluble in the usual organic solvents with the exception of petroleum (b. p. 60—80°) (Found : C = 65·4; H = 4·2%).

3 : 5-*Dinitro*-o-*tolyl benzoate*, $C_6H_2Me(NO_2)_2{\cdot}OBz$, m. p. 132°, prepared in a similar manner from sodium 3 : 5-dinitro-*o*-tolyl oxide, crystallises readily from acetone, alcohol, or benzene; it is sparingly soluble in alcohol, ether, or light petroleum, but easily soluble in acetone, benzene, chloroform, or carbon tetrachloride (Found : C = 55·7; H = 3·4. $C_{14}H_{10}O_6N_2$ requires C = 55·6; H = 3·3%).

The Toluene-p-*sulphonyl Derivatives.*—5-*Nitro*-o-*tolyl toluene*-p-*sulphonate*, $NO_2{\cdot}C_6H_3Me{\cdot}O{\cdot}SO_2{\cdot}C_7H_7$, obtained as in the case of the corresponding benzoate (p. 46), using toluene-*p*-sulphonyl chloride, crystallises from alcohol, petroleum (b. p. 60—80°), or carbon tetrachloride in indefinite plates, m. p. 107°. It is sparingly soluble in alcohol or light petroleum, but fairly soluble in acetone, benzene, chloroform, or carbon tetrachloride (Found : S = 10·5. $C_{14}H_{13}O_5NS$ requires S = 10·4%).

3-*Nitro*-o-*tolyl toluene*-p-*sulphonate* was prepared by treating sodium 3-nitro-*o*-tolyl oxide (1 mol.) with pure toluene-*p*-sulphonyl chloride (2 mols.) : * the conditions and method of isolation were the same as those described in the case of the benzoate (p. 46).

The compound melts at 66° and boils at 257°/11 mm. with decomposition, but distils unchanged at 205—210°/0·5 mm.; it crystallises well from alcohol, in which it is sparingly soluble, and dissolves freely in acetone, benzene, chloroform, or carbon tetrachloride (Found : S = 10·2%).

The corresponding toluene-*p*-sulphonate from 3 : 5-dinitro-*o*-cresol, which has already been isolated by Ullmann and Sané (*Ber.*, 1911, **44**, 3730), can be prepared in a similar manner.

3-Nitro-*o*-chlorotoluene is formed in very small quantities by the action of benzoyl or toluene-*p*-sulphonyl chloride on sodium 3-nitro-*o*-tolyl oxide and can be isolated by steam distillation of the crude reaction mixture, when a pale yellow, pleasant-smelling oil passes over (compare Holleman, *Rec. trav. chim.*, 1908, **27**, 456).

In a similar manner, sodium 3 : 5-dinitro-*o*-tolyl oxide yields the corresponding 3 : 5-dinitro-*o*-chlorotoluene (m. p. 63°), which was oxidised to 3 : 5-dinitro-*o*-chlorobenzoic acid (m. p. 238°).

The Methyl Ethers.—5-Nitro-*o*-tolyl methyl ether, m. p. 64° (Cain and Simonsen, J., 1914, **105**, 2390, give m. p. 62°), crystallises readily in needles from alcohol or petroleum, but is freely soluble in acetone, chloroform, carbon tetrachloride, or benzene. On

* The commercial compound was dried in a vacuum at 100° and dissolved in hot petroleum (b. p. 60—80°), the tarry material filtered off, the solvent removed, and the residue distilled under reduced pressure; b. p. 138—139°/9 mm.

oxidation with boiling dilute permanganate, 5-nitro-*o*-methoxybenzoic acid (m. p. 150°) was obtained in theoretical yield.

3-Nitro-*o*-tolyl methyl ether was obtained by heating sodium 3-nitro-*o*-tolyl oxide (1 mol.) at 120° with pure methyl sulphate (2 mols.) for 2 hours. The dark-coloured reaction mixture was submitted to distillation in steam, the volatile oil extracted with ether, and the 3-nitro-*o*-cresol removed with dilute alkali. The ethereal solution was evaporated, the residue distilled under 10 mm., and the product (b. p. 121—122°) dissolved in petroleum (b. p. 60—80°); at −15°, the solution deposited 3-nitro-*o*-tolyl methyl ether in large needles, m. p. 30°.

The residue from the steam distillation of the methyl ether, treated with calcium carbonate, gave a mixture of calcium nitrocresolsulphonates (p. 43) together with sodium carbonate, but the acids could not be separated by the fractional crystallisation of various inorganic and organic salts which were tried.

3 : 5-Dinitro-*o*-tolyl methyl ether (m. p. 72°) can be prepared under the conditions just described; the yield is good. 3-Nitro-*o*-tolyl methyl and ethyl ethers and the corresponding methyl and ethyl derivatives of 3 : 5-dinitro-*o*-cresol were also prepared by heating the requisite dry sodium salts with methyl or ethyl toluene-*p*-sulphonate * in a similar manner. The yields were good, and the products had the properties given in the literature.

In conclusion, the author desires to express his thanks to the Department of Scientific and Industrial Research for a grant which enabled him to carry out the above work, and to Professor F. S. Kipping for his kindly supervision.

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VIII.—*Limits for the Propagation of Flame in Inflammable Gas–Air Mixtures. Part II. Mixtures of More than One Gas and Air.*

By ALBERT GREVILLE WHITE.

LE CHATELIER has put forward a formula connecting the limit for the propagation of flame in a mixture containing two inflammable

* Pure toluene-*p*-sulphonyl chloride (50 g.; p. 47) was suspended in methyl (or ethyl) alcohol (100 c.c.), well-stirred, and 20% caustic soda (10% in excess of 1 mol.) gradually added with cooling; the oil which took the place of the solid was separated with ether, and the extract was washed with water, dried with sodium sulphate, and evaporated. The residue was crystallised from alcohol at −15°. B. p. of methyl ester, 146—147°/9 mm.; of ethyl ester, 165—166°/9 mm.

gases and air with the limits for the two inflammable gases taken separately. When generalised, it becomes

$$n_1/N_1 + n_2/N_2 + n_3/N_3 + \ldots\ldots = 1,$$

where n_1, n_2, n_3, . . . are the percentages of different combustibles found in the final limit mixture, and N_1, N_2, N_3, . . . are the percentages of the same combustibles required to give limit mixtures when each is mixed separately with air. The formula is additive in character, and indicates that if any number of limit mixtures are mixed, the resulting mixture will be a limit mixture. It is simple, but unlikely to be universally true.

It has been shown (J., 1922, **121**, 2561) that the formula enables the lower limits of binary mixtures to be calculated fairly accurately from the limits of the pure vapours, except for mixtures containing carbon disulphide, where agreement over a portion of the range was only obtained when an artificial figure was used for the limit of carbon disulphide. At the upper limit of downward propagation the mixtures also followed Le Chatelier's rule, except mixtures containing carbon disulphide, but notable discrepancies were sometimes found for other directions of propagation. These could be traced to anomalous behaviour of one of the vapours. Thus the formula was clearly inapplicable to a vapour giving a cool flame, and by the suitable choice of a second vapour the propagation range of ether–second vapour–air was divided into two, the mixtures having thus four limits instead of two.

Coward, Carpenter, and Payman (J., 1919, **115**, 27, 31), who deal only with propagation upwards, conclude that the limits of inflammability, in air, of mixtures of hydrogen, carbon monoxide and methane, taken two at a time or all together, as well as the limits of coal gas, may be calculated by using Le Chatelier's formula. Other workers have drawn the same conclusion, but since the amount of experimental work was small, further experiments appeared to be desirable, as any radical departure from the formula might throw light on the method of propagation at the limit of the individual gases used.

The experimental arrangements were identical with those used previously (J., 1924, **125**, 2387), except that the tubes were 5 cm. in diameter unless some other size is specified. The work was all carried out within the range of 17° ± 4°, and usually between 15° and 19°. The results are given in Tables I and II. Limits are given as percentages by volume throughout, and percentage errors are calculated as percentages of the amount of inflammable gas in the limit mixture.

Table I.

Showing the ranges of propagation of flame for mixtures of pairs of inflammable gases and air, and the deviations from Le Chatelier's formula.

Composition of combustible in mixture by vol.		Upward propagation.				Downward propagation.			
		Range.		% Deviation at		Range.		% Deviation at	
% H_2.	% CH_4.	Found.	Calc.	Lower limit.	Upper limit.	Found.	Calc.	Lower limit.	Upper limit.
0	100	5·40 to 14·25	—	—	—	6·12 to 13·25	—	—	—
10	90	5·50 to —	5·24 to —	− 5	—				
25	75	4·75 to 18·5	5·02 to 17·9	+ 6	− 3	6·75 to 16·5	6·65 to 16·7	− 1	+ 1
50	50	4·45 to 26·1	4·69 to 23·9	+ 5	− 8	7·35 to 22·3	7·29 to 22·5	− 1	+ 1
75	25	4·15 to 38·3	4·40 to 36·2	+ 6	− 6	8·10 to 34·3	8·05 to 34·5	− 1	+ 1
100	0	4·15 to 74·5	—	—	—	9·00 to 74·0	—	—	—
% H_2.	% NH_3.								
0	100	16·1 to 26·6	—	—	—	—	—	—	—
25	75	8·65 to 34·5	9·36 to 31·7	+ 8	− 8	16·2 to 30·5	*22·1 to *25·5		
50	50	6·10 to 45·2	6·60 to 39·2	+ 8	−13	12·5 to 41·0	*20·5 to *28·4		
75	25	4·75 to 57·0	5·10 to 51·4	+ 7	−10	10·5 to 55·2	*21·0 to *31·3		
100	0	4·15 to 74·5	—	—	—	9·00 to 74·0	—	—	—
% C_2H_4.	% H_2.								
0	100	4·15 to 74·5	—	—	—	9·00 to 74·0	—	—	—
5	95	— to 56·0	— to 70·2	—	+25				
10	90	4·00 to —	4·02 to —	0	—	7·95 to —	7·74 to —	− 3	—
25	75	3·95 to 42·0	3·84 to 56·9	− 3	+35	6·85 to 34·0	6·39 to 37·8	− 7	+11
50	50	3·70 to 36·5	3·57 to 46·0	− 4	+26	5·35 to 23·5	4·96 to 25·4	− 7	+ 8

Composition of combustible in mixture. by vol.		Upward propagation.				Downward propagation.			
		Range.		% Deviation at		Range.		% Deviation at	
% C_2H_4.	% H_2.	Found.	Calc.	Lower limit.	Upper limit.	Found.	Calc.	Lower limit.	Upper limit.
75	25	3·45 to 33·5	3·33 to 38·6	− 3	+15	4·15 to 18·9	4·05 to 19·1	− 2	+ 1
100	0	3·13 to 33·3	—	—	—	3·42 to 15·3	—	—	—
% C_2H_2.	% H_2.								
0	100	4·15 to (4·15)	—	—	—	9·00 to —	—	—	—
25	75	3·55 to (3·50)	3·60 to —	+ 2	—	6·02 to —	5·79 to —	− 4	—
40	60	3·34 to —	3·35 to —	0	—				
50	50	3·24 to (3·20)	3·19 to —	− 2	—	4·42 to —	4·27 to —	− 3	—
57	43	3·49 to —	3·10 to —	−11	—				
60	40	— to (3·39)	—	—	—				
65	35	3·32 to —	2·99 to —	−10	—				
75	25	3·11 to (3·12)	2·87 to —	− 8	—	3·40 to —	3·38 to —	− 1	—
85	15	2·93 to —	2·76 to —	− 6	—				
100	0	2·60 to (2·60)	—	—	—	2·80 to —	—	—	—
% C_2H_4.	% CH_4.								
0	100	5·40 to 14·25	—	—	—	6·12 to 13·25	—	—	—
25	75	4·75 to 16·1	4·57 to 16·6	− 4	+ 3	5·23 to 13·7	5·11 to 13·7	− 2	0
50	50	4·22 to 19·5	3·96 to 20·0	− 6	+ 3	4·55 to 14·0	4·39 to 14·2	− 4	+ 1
75	25	3·72 to 25·0	3·50 to 25·0	− 6	0	4·05 to 14·8	3·84 to 14·7	− 5	− 1
100	0	3·13 to 33·3	—	—	—	3·42 to 15·3	—	—	—

The figures in brackets in Table I are lower-limit determinations carried out in tubes 7·5 cm. in diameter. Those marked with an asterisk are the values of the propagation range downwards for ammonia–air mixtures as calculated from the ranges found for the various ammonia–hydrogen–air mixtures.

Table II.

Showing the ranges of propagation of flame for mixtures of pairs of inflammable gases and air, and the deviations from Le Chatelier's formula.

Composition of combustible in mixture by vol.		Upward propagation.				Downward propagation.			
		Range.		% Deviation at		Range.		% Deviation at	
% CH_4.	% H_2S.	Found.	Calc.	Lower limit.	Upper limit.	Found.	Calc.	Lower limit.	Upper limit.
0	100	4·40 to 44·5	—	—	—	6·05 to 19·8	—	—	—
10	90	5·15 to —	4·48 to —	−13	—	6·50 to —	6·06 to —	− 7	—
15	85	— to 36·3	— to 33·8	—	− 7	—	—	—	—
25	75	5·75 to 33·0	4·61 to 29·1	−20	−12	6·90 to 19·1	6·07 to 17·6	−12	− 8
40	60					— to 17·2	— to 16·5	—	− 4
50	50	6·03 to 28·8	4·85 to 21·6	−20	−25	7·00 to 15·9	6·08 to 15·9	−13	0
60	40	— to 26·1	— to 19·6	—	−25				
65	35					— to 14·2	— to 15·0	—	+ 6
67·5	32·5	— to 18·6	— to 18·3	—	− 2				
75	25	5·80 to 15·7	5·11 to 17·2	−12	+10	6·75 to 13·6	6·10 to 14·4	−10	+ 6
100	0	5·40 to 14·25	—	—	—	6·12 to 13·25	—	—	—
% H_2S.	% H_2.								
0	100	4·15 to 74·5	—	—	—	9·0 to 74·0	—	—	—
10	90					— to 50·0	— to 58·1	—	+16
15	85	— to 46·0	— to 67·7	—	+47	— to 45·5	— to 52·5	—	+15
25	75	4·27 to 41·3	4·21 to 63·8	− 1	+54	8·43 to 38·7	8·02 to 43·9	− 5	+13
50	50	4·78 to 40·0	4·27 to 55·7	−11	+39	7·85 to 29·0	7·24 to 31·2	− 8	+ 8

Composition of combustible in mixture by vol.		Upward propagation.				Downward propagation.			
		Range.		% Deviation at		Range.		% Deviation at	
% H_2S.	% H_2.	Found.	Calc.	Lower limit.	Upper limit.	Found.	Calc.	Lower limit.	Upper limit.
75	25	5·03 to 40·4	4·34 to 49·5	−14	+23	6·95 to 23·0	6·59 to 24·2	− 5	+ 5
90	10	4·72 to —	4·37 to —	− 7	—				
100	0	4·40 to 44·5	—	—	—	6·05 to 19·8	—	—	—
% H_2S.	% C_2H_2.								
0	100	2·60 to —	—	—	—	2·80 to —	—	—	—
25	75	2·99 to —	2·90 to —	− 3	—	3·23 to —	3·23 to —	0	—
50	50	3·44 to —	3·27 to —	− 5	—	3·88 to —	3·83 to —	− 1	—
75	25	4·04 to —	3·75 to —	− 7	—	4·80 to —	4·69 to —	− 2	—
90	10	4·36 to —	4·11 to —	− 6	—				
100	0	4·40 to —	—	—	—	6·05 to —	—	—	—
% C_2H_2.	% CH_4.								
0	100	5·40 to 14·25	—	—	—	6·12 to 13·25	—	—	
10	90	— to 15·7	— to 15·5	—	− 1				
25	75	4·40 to 23·4	4·25 to 17·9	− 3	−24	4·85 to 15·7	4·72 to 16·5	− 3	+ 5
30	70	— to 39·5	— to 18·9	—	−52				
40	60	— to 47·0	— to 21·2	—	−55				
50	50	3·67 to 47·0	3·51 to 24·1	− 4	−49	3·98 to 20·4	3·84 to 21·9	− 4	+ 7
75	25	3·07 to 58·0	2·99 to 36·8	− 3	−37	3·27 to 31·2	3·24 to 32·6	− 1	+ 4
100	0	2·60 to 78·0	—	—	—	2·80 to 63·5	—	—	—

Composition of combustible in mixture. by vol. % CH_4.	% C_5H_{12}.	Upward propagation. Range. Found.	Calc.	% Deviation at Lower limit.	Upper limit.	Downward propagation. Range. Found.	Calc.	% Deviation at Lower limit.	Upper limit.
0	100	1·43 to 8·00	—	—	—	1·49 to 4·56	—	—	—
20	80	— to 8·85	— to 8·77	—	− 1				
25	75	1·75 to —	1·75 to —	0	—	1·84 to 5·30	1·84 to 5·45	0	+ 3
50	50	2·23 to 9·65	2·26 to 10·25	+ 1	+ 6	2·38 to 6·50	2·40 to 6·78	+ 1	+ 4
75	25	3·15 to 11·35	3·19 to 11·92	+ 1	+ 5	3·47 to 8·75	3·45 to 8·98	− 1	+ 3
100	0	5·40 to 14·25	—	—	—	6·12 to 13·25	—	—	—

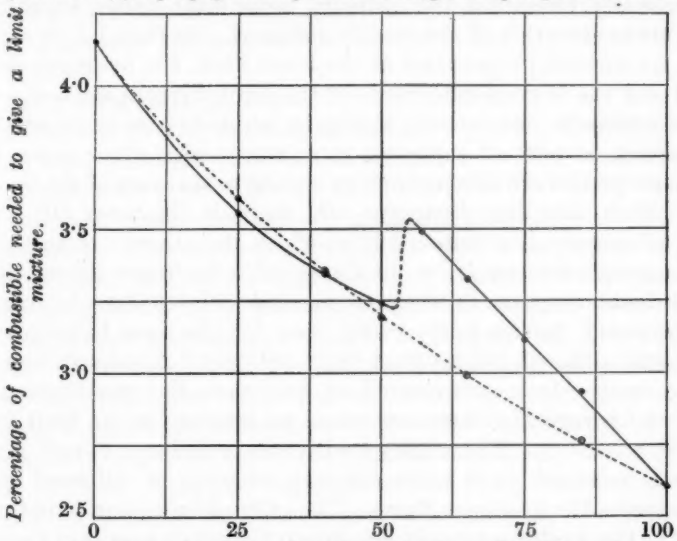
Discussion of Results.

The figures of Table I show that for propagation downwards the deviations from Le Chatelier's rule are not important except for hydrogen–ethylene–air and hydrogen–ammonia–air mixtures. Hydrogen and ethylene appear to hinder one another's burning at the limit, as the calculated range is wider than that observed. The results for propagation upwards show that at both upper and lower limits the presence of hydrogen makes propagation easier than might have been expected when the second inflammable gas is methane or ammonia. This does not apply to mixtures containing acetylene or ethylene, the discrepancies shown by the upper-limit figures for mixtures of the latter being striking. The corresponding deviations at the lower limit are small, but when considered in conjunction with the corresponding ones for mixtures containing methane or ammonia, they appear to indicate a distinct hindering effect when either ethylene or acetylene is mixed with hydrogen at the limit. In addition, a somewhat curious change of sign occurs for the deviations from Le Chatelier's rule at the lower limit in both methane–hydrogen–air and acetylene–hydrogen–air mixtures. Thus in Fig. 1, which shows the lower-limit figures observed and calculated for the latter mixtures, the experimental curve consists of two parts, one portion, representing mixtures containing an excess of hydrogen, being slightly below, and the other portion distinctly above, the curve of calculated values. When the percentage of acetylene in the combustible gas in the limit

mixture is changed from 50% to 57%, the limit rises from 3·24% to 3·49%, despite the fact that the limit for acetylene is considerably lower than that for hydrogen. Considerable difficulty was experienced in determining the limit for the 50% mixture. Mixtures containing an amount of combustible not less than 3·24% sometimes propagated flame throughout the length of the tube, whilst mixtures containing more than 3·24% but less than 3·40% often failed to do so. The difficulty, which was also encountered, although in a less degree, when determining the corresponding limit for the

FIG. 1.

Showing the lower limits observed (full line) and calculated from Le Chatelier's rule (dotted line) for propagation upwards in acetylene–hydrogen–air mixtures.



mixture containing 75% of methane and 25% of hydrogen, was overcome in each case by making numerous trials with each mixture and taking as the limit mixture that containing least combustible in which a flame was propagated throughout the tube, despite the fact that a mixture containing the same percentage, or even a greater percentage of combustible, had failed to propagate flame; if one of several similar mixtures propagated flame farther than the others, that mixture was always burning with a flame more closely resembling that of hydrogen than the others. It is thus apparently only when initiated so as to give the hydrogen type of flame that the true limit mixture propagated flame. The analogy with the state of things sometimes found when a cool flame can be propagated

in certain mixtures is at once seen. In the latter case, an ordinary flame goes out during its passage along a limit tube, whilst a cool flame always reaches the far end. When a tube 7·5 cm. in diameter was used, there was little difficulty in producing the hydrogen type of flame every time in the mixtures referred to above, and the limits obtained provided useful confirmation of those obtained in 5 cm. tubes. The values in brackets (7·5 cm. tubes) in Table I. show that the difference between the 5 cm. and the 7·5 cm. results is nowhere important. The agreement for methane–hydrogen–air mixtures was just as good. The observation that the flame for mixtures shown along part of the curve in Fig. 1 was always of the hydrogen type, whilst that found for those on the other portion more nearly resembled the ordinary lower-limit flame, suggests a possible explanation of the results obtained. In Part I it is shown that, for upward propagation at the lower limit, the hydrogen flame itself and the low calorific value of the limit mixture are quite out of the ordinary. Apparently hydrogen is able to pass on its peculiar properties, in part at any rate, to mixtures with other gases, but these properties are damped out by excessive amounts of the second gas. With acetylene–hydrogen–air, there is, between 50% and 57% of acetylene, a limit—that at which the amount of acetylene becomes sufficient to damp out the peculiar hydrogen flame. This point does not appear to be clearly marked with ethylene–hydrogen–air mixtures, but is fairly easily seen for methane–hydrogen–air mixtures, although the range of the " ordinary " flame here appears to be small. It is unexpected to find that the substitution of 10% of hydrogen for methane causes an increase in the limit from 5·40% to 5·50%. The analogy with the cool flame is well maintained, inasmuch as it takes differing amounts of different gases to suppress the hydrogen flame. That the phenomenon is not confined to the mixtures examined is shown by certain results of Coward and his collaborators (*loc. cit.*). They state: " The most striking anomaly was shown by the mixture containing 10 per cent. of hydrogen and 90 per cent. of carbon monoxide, where the large difference was in the opposite direction to that normally noted," but suggest no explanation.

The second part of the acetylene–hydrogen–air curve is so distinct from the first as to lead one to attempt to obtain from it some idea as to what the lower limit upwards would be for hydrogen if its own peculiar flame could be suppressed. Assuming Le Chatelier's rule to hold and making use of the value for 75% of acetylene and 25% of hydrogen, a figure between 7 and 8% is obtained. This is reasonably near the value for propagation downwards, but little reliance can be placed on it for two reasons. In the first place

Le Chatelier's rule is not followed closely by these gases even for propagation downwards, and, in the second, a different and lower value would be obtained by using the figures for methane–hydrogen–air. Nevertheless, any figures obtained by extrapolation would be likely to be minimum values, so that the figure is certainly suggestive.

As ammonia does not propagate flame downwards at the ordinary temperature, the ammonia–hydrogen–air values have been utilised to calculate hypothetical values for the ammonia limits. The lower-limit results are reasonably near one another, but there is a large increase observable in the upper-limit values as the percentage of hydrogen in the mixture increases. The values obtained appear to point to the fact that for downward propagation at the upper limit considerable deviations from Le Chatelier's rule take place for these mixtures, the experimental values being greater than those calculated.

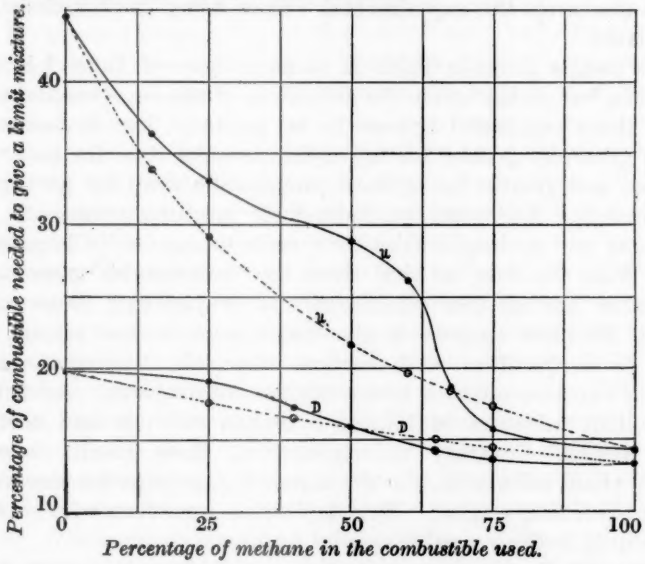
The results given in Table II confirm those of Table I in many respects, but on the whole the deviations of the experimental values from those calculated appear to be greater. The deviations are again generally greater for upper-limit results than for lower-limit figures, and greater for upward propagation than for propagation downwards. The work on lower-limit mixtures containing both methane and hydrogen sulphide reveals unexpectedly large deviations from the rule, so that these two inflammable gases appear to hinder one another considerably in propagating flame at the limit. Methane appears to give much more normal results when used in conjunction with carbon monoxide, hydrogen, certain organic vapours, and even with acetylene and ethylene. Accordingly lower-limit mixtures containing hydrogen sulphide and acetylene were tested. Contrary to expectation, these results were far nearer those calculated, the deviations for propagation downwards being exceedingly small. Fair deviations were found for mixtures containing hydrogen sulphide and hydrogen.

The upper-limit results are best examined from the point of view of the curves shown in Figs. 2 to 4, which show both experimental and calculated values. The deviations of the experimental from the calculated values for methane–hydrogen sulphide–air mixtures (Fig. 2) are sometimes large, but the most interesting point is the fact that for both directions of propagation the experimental and theoretical curves cut one another. For downward propagation, about as much of the experimental curve lies above the theoretical as below, but this is not the case for upward propagation. It should also be noticed that whilst the addition of some methane to a hydrogen sulphide–air mixture hinders propagation at the lower limit, it seems to promote propagation at the upper limit.

The values for hydrogen sulphide–hydrogen–air mixtures show that for both upper and lower limit mixtures these gases propagate flame relatively more easily singly than when both are present in a mixture. Fig. 3 shows that at the upper limit this effect is much more marked for upward than for downward propagation. For mixtures in which more than 80% of the combustible is hydrogen, the limits for both directions of propagation are almost identical, but for mixtures poorer in hydrogen the two curves are quite different. The experimental and the theoretical curves are of very

FIG. 2.

Showing the upper limits observed (full line) and calculated from Le Chatelier's rule (dotted line) for methane–hydrogen sulphide–air mixtures. D *denotes downward propagation,* U *propagation upwards.*

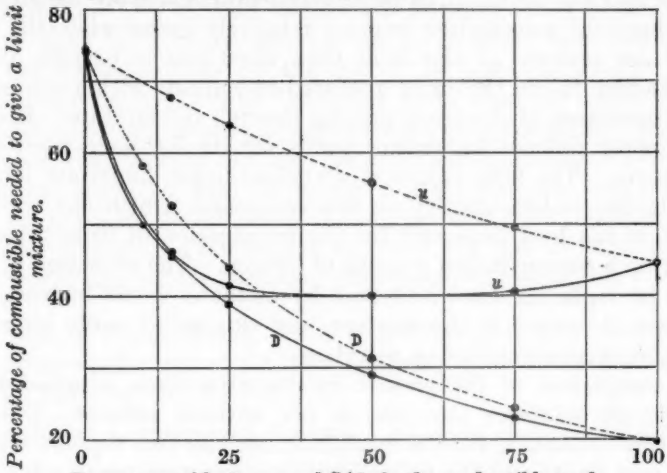


similar form for propagation downwards, but for upward propagation the major portion of the experimental curve is nearly horizontal. Experimental difficulty was encountered when the upper limit was being determined for mixtures in which 75% of the inflammable gas was hydrogen and the remainder hydrogen sulphide. The limit figure obtained was dependent on the flame starting up the tube, the type of flame being presumably controlled by the igniting mechanism. It was difficult to control efficiently the type of flame produced, and the limit figure was determined as in the case of acetylene–hydrogen–air mixtures (p. 55).

The values for the upper limit for methane–acetylene–air mixtures

FIG. 3.

Showing the upper limits observed (full line) and calculated from Le Chatelier's rule (dotted line) for hydrogen sulphide–hydrogen–air mixtures. D *denotes downward propagation,* U *propagation upwards.*



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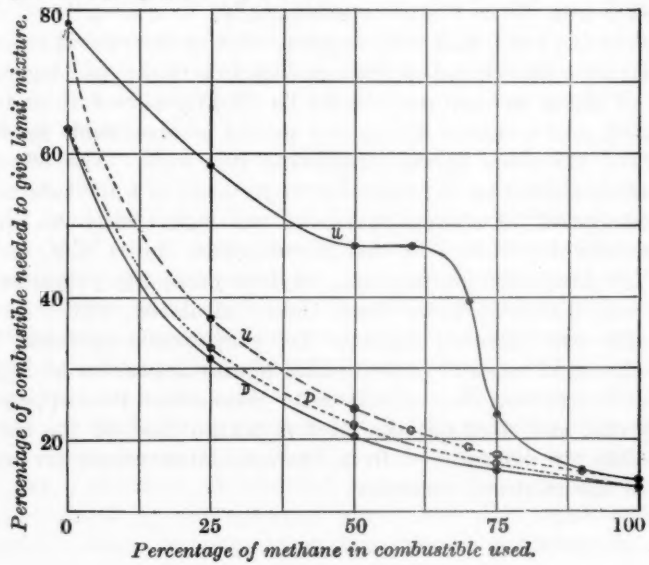

(Fig. 4) are not far from those calculated for downward propagation, the latter being always the greater. For upward propagation, the differences between the two sets of results are far greater, and are in the opposite direction, as the experimental figures are the greater, showing that propagation appears relatively easier when the two gases are present at the limit than when one is burning alone. The sudden fall in the curve appeared to coincide with a change in the appearance of the flame passing through the mixture. It does not appear difficult to account partly for the left-hand portion of the curve. The high values of acetylene upper limits are largely due to the endothermicity of this compound, which can provide much of the heat necessary for the propagation of flame without using up a corresponding amount of oxygen. The reduction of the limit on replacing some acetylene by methane would increase the amount of oxygen in the mixture, and this might easily intensify the abnormal effect due to acetylene.

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Payman (J., 1923, **123**, 412) suggests that as the rate of reaction in a mixture must depend on the concentration of the reacting gases, speeds of flame in mixtures should be slightly slower than those calculated, and a similar divergence should be observable for limit mixtures. He gives figures supporting this view. The effect of mass action should be to reduce the upper limit of a mixture below that calculated. An examination of the eight series of upper-limit results determined in this investigation shows that, in the main, for downward propagation, in four cases the experimental figures are distinctly lower than those calculated, whilst in one series they are distinctly higher. For propagation upwards, four out of the eight series of experimental figures appear to be higher, and four lower, than those calculated. Mass action thus appears to be only one, and often not the most important one, of the factors responsible for divergencies from the calculated values for upper limits in the mixtures examined.

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The deviations from this rule are considerably greater for the gas mixtures examined than for normal vapour mixtures, but no rule can be given for the direction of the deviation from the calculated values. For gas, as for vapour mixtures, the *type* of flame started sometimes determines whether propagation occurs or no.

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IX.—*Solubility of Bi-bivalent Salts in Solutions Containing a Common Ion.*

By OSWALD JAMES WALKER.

THE investigation of the solubility of salts in dilute solutions of salts with common ions has been confined mainly to the following cases: 1. Uni-univalent salt + univalent common ion. 2. Uni-bivalent salt + univalent common ion. 3. Uni-bivalent salt + bivalent common ion.

It was shown by Noyes and his co-workers (*J. Amer. Chem. Soc.*, 1911, **33**, 1643, 1807) that in cases (1) and (2) the solubility decreases rapidly, and the curve obtained by plotting solubility against concentration of added salt is roughly of the form to be expected from the solubility product principle. In case (3), where a salt with a common bivalent ion is added, the decrease in solubility is much less than what would be expected from that principle, and if the saturating salt is sufficiently soluble the common ion may actually bring about an increase in the solubility. Fewer cases have been studied in which the saturating salt is bi-bivalent, and such cases as have been examined (*e.g.*, Harkins and Paine, *J. Amer. Chem. Soc.*, 1919, **41**, 1162) have shown that here also the solubility decrease brought about by the common ion is less than what would be expected. More recently there has been a tendency to reject

the conductivity method of calculating ionic concentrations, which was the method used in applying the solubility product principle, and the question of solubility effects has been approached from a different point of view based on thermodynamic considerations which involve the principles of the inter-ionic attraction theory.

With a view to get further evidence concerning the solubility effects in the system bi-bivalent salt + bivalent common ion, the solubilities of several salts have been investigated. For this purpose, the succinates and malonates of the alkaline-earth metals afford a suitable range of concentrations. The solubilities of the various salts considered, expressed in gram-molecules per 1000 grams of water, varied between 0·016 and 0·082 weight molar, whilst the total salt concentration did not exceed 0·1 weight molar, except in the case of calcium succinate as saturating salt, with which a maximum of about 0·3 weight molar was reached.

Experimental.

The saturating salts were prepared from pure reagents by precipitation, thorough washing, and drying at the temperature requisite to give the anhydrous salt. Sodium and magnesium succinates were obtained by crystallisation from neutralised succinic acid solutions and were recrystallised several times. Analysis confirmed the purity of the salts thus obtained.

The solubility determinations were carried out in 100 c.c. Jena conical flasks, closed with rubber stoppers and provided with rubber caps. Excess of the saturating salt and a weighed quantity of the other salt were added to a known weight of water in the flask, and the mixture was rotated in a thermostat kept at 25° ± 0·1° until equilibrium had been reached (about 30 hours). The solution, after standing in the thermostat for an hour, was filtered upward by suction through a small filter paper into a weighed flask, which was also in the thermostat. After weighing, the solution was carefully washed out into a beaker and the solubility was obtained by determining gravimetrically the amount of the metallic radical of the saturating salt. Barium was estimated in most cases as sulphate, but in presence of calcium, Browning's method (*Amer. J. Sci.*, 1892, [iii], **43**, 314), depending on the difference in solubility of the nitrates in amyl alcohol, was employed. Calcium was precipitated as oxalate and weighed as sulphate, the precipitation, in presence of magnesium, being carried out twice. Strontium was precipitated as carbonate and weighed as sulphate. In the case of strontium malonate + strontium chloride, the chloride in the solution was determined gravimetrically as silver chloride, and the amount of strontium as malonate was determined by subtraction of

the strontium present as chloride from the total strontium. Independent solubility determinations gave results agreeing within 0·5%.

The results are shown in Table I, s being the solubility, expressed in gram-molecules per 1000 grams of water, corresponding to the weight-molar concentration, c, of added salt; s_0 is the solubility

TABLE I.

s.	c.	s.	c.	s.	c.
Ba succ. + Na succ. $s_0 = 0{\cdot}01570$.		Sr mal. + $SrCl_2$. $s_0 = 0{\cdot}03050$.		Ba succ. + Mg succ. $s_0 = 0{\cdot}01570$.	
0·01307	0·00798	0·02523	0·01828	0·01397	0·00770
0·01154	0·01575	0·02349	0·03103	0·01294	0·01538
0·00987	0·03149	0·02019	0·06149	0·01155	0·03074
0·00913	0·04726			0·01065	0·04620
				0·01024	0·06149
Sr succ. + Na succ. $s_0 = 0{\cdot}02013$.		Ca succ. + Na succ. $s_0 = 0{\cdot}08252$.		Ba succ. + Ca succ. $s_0 = 0{\cdot}01570$.	
0·01740	0·00938	0·08013	0·00826	0·01383	0·00798
0·01535	0·01875	0·07103	0·0506	0·01275	0·01597
0·01322	0·03751	0·06495	0·1014	0·01155	0·03193
0·01221	0·05582	0·06138	0·1526		
0·01143	0·07457	0·05759	0·2560		

Calcium succinate + Magnesium succinate. $s_0 = 0{\cdot}08252$.

s	0·07769	0·07474	0·07340	0·07173	0·07087
c	0·04121	0·06179	0·08230	0·1231	0·1631

of the saturating salt in pure water. The solubility effects, however, can be more easily compared by means of the ratios s/s_0 and c/s_0, which express respectively the concentrations of the saturating salt and of the added salt in terms of the solubility of the former in pure water. These ratios correspond to the terms "fractional solubility" and "fractional concentration" employed by Harkins (*J. Amer. Chem. Soc.*, 1911, **33**, 1851). In Figs. 1 and 2, the values of s/s_0 are plotted against the values of c/s_0, for the addition respectively of uni-bivalent and bi-bivalent salt. For comparison, a typical curve for the system uni-univalent salt + univalent common ion (silver propionate + sodium propionate, Arrhenius, *Z. physikal. Chem.*, 1899, **31**, 225) is also shown (dotted curve).

The curves all lie considerably above the curve for the uni-univalent salt, and for any one saturating salt the curve of Fig. 2 lies above that of Fig. 1. Moreover, for one type of added salt, the curves all lie in the order of the solubility of the saturating salt in pure water, the curve taking a higher position the greater the solubility; this order was found to hold by Harkins (*loc. cit.*) for the salts investigated by him. The lowering effects of calcium and magnesium succinates on the solubility of barium succinate are almost equal, the crosses on curve 2 (Fig. 2) denoting addition of calcium succinate.

Noyes (*J. Amer. Chem. Soc.*, 1924, **46**, 1080, 1098), in his critical presentation of the interionic attraction theory of ionised solutes as put forward by Milner (*Phil. Mag.*, 1912, [vi], **23**, 551; 1913, **25**, 742) and by Debye and Hückel (*Physikal. Z.*, 1923, **24**, 185), uses some of the existing data on the solubility of salts in salt solutions in order to test the validity of the theory. He finds that the solubility effects should be given by an equation, which takes the follow-

Fig. 1.

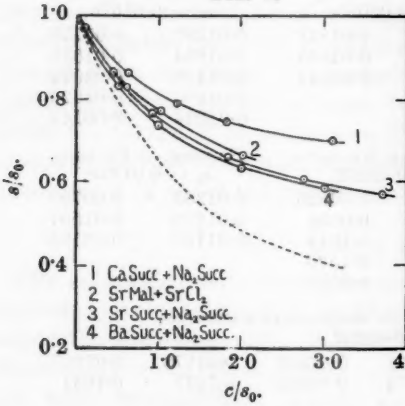
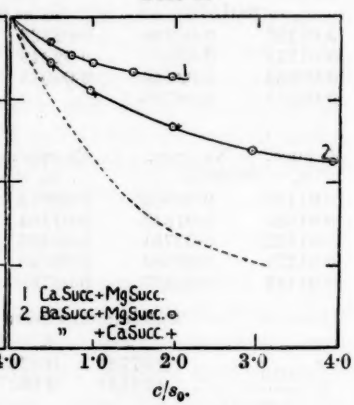


Fig. 2.



ing form for bi-bivalent saturating salts, s_0, s, and c being the concentration terms hitherto employed in this paper,

$$\tfrac{1}{8}\log\frac{s(s+c)}{{s_0}^2} = \alpha(\sqrt{\Sigma c'\nu^2} - \sqrt{8s_0}),$$

where α has the theoretical value of 0·357 for dilute solutions at 25°. $\Sigma c'\nu^2$ denotes the summation of ion concentration (c') × square of valence of ion (ν^2) for all the ions present, half this quantity representing the "ionic strength" as defined by Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1140). In Table II are shown the values of the coefficient for the two least soluble salts, barium succinate and strontium succinate, calculated from the solubility data in Table I. The values for the system calcium sulphate + magnesium sulphate calculated from the data quoted in Noyes's paper are also shown.

The values in each column are arranged in order of increasing total salt concentration, and it will be seen that in this order α in most cases decreases, reaching a value of about 0·15 at ionic strengths between 0·2 and 0·45 molar. The data for the case of calcium succinate as saturating salt, a salt about four times as soluble as any of the saturating salts in Table II, give even smaller values of α, about 0·09 in the most concentrated solutions. Whilst

TABLE II.

Values of α.

"Ionic strength." $\frac{1}{2}\Sigma c'\nu^2$.	Ba succ. + Mg succ. $s_0=0{\cdot}01570$.	Ba succ. + Ca succ. $s_0=0{\cdot}01570$.	Ba succ. + Na succ. $s_0=0{\cdot}01570$.	Sr succ. + Na succ. $s_0=0{\cdot}02013$.	$CaSO_4$ + $MgSO_4$. $s_0=0{\cdot}01517$.
0·08	0·181	0·173	0·165	0·186	0·201
to	0·177	0·172	0·171	0·166	0·196
0·20	0·164	0·164	0·168	0·158	0·181
0·20	0·153		0·165	0·152	0·169
to					
0·45	0·147			0·145	0·150

the values of α in the first three rows of the table are constant to within about 10%, they are still somewhat smaller than the value 0·238, which Noyes finds to satisfy the experimental facts up to ionic strengths of 0·1*M* in the case of the three salts of higher valence type quoted by him. The differences in the values of α from one another are greater than those which could be due to experimental error in the value of the solubility. An error in the latter as great as 1% (the actual maximum error was about 0·5%) makes a difference of about 5% in the values of α.

Although α increases with decreasing salt concentration, extrapolation from the graph obtained by plotting concentration against the corresponding values of α does not show any tendency for α to reach a value as high as 0·357, even at very small concentrations. In order, therefore, to obtain data at much smaller concentrations than those employed so far in this paper, some experiments were carried out on the solubility of barium and magnesium oxalates in presence of barium chloride and magnesium sulphate respectively. It was hoped that the results of these experiments would give an indication of the value of the "constant" α in Noyes's equation at these much smaller concentrations (about 0·003 to 0·0006 weight-molar), for which the equation ought to hold more closely than in the cases already dealt with. The solubility was determined in each case by titration of the amount of oxalate present in about 200 g. of solution with carefully standardised permanganate solution of such a strength that from 30—60 c.c. were used up in the titration.

From these results, no consistent value for α was obtained in the case of barium oxalate. At small concentrations corresponding to the solubility of barium oxalate, a small error in the experimentally obtained value of the solubility becomes highly magnified in the calculation of α, which may consequently vary enormously. With the more soluble magnesium salt, the influence of an experimental error is not so marked, an error of 1·0% in the solubility causing an error of about 5% in the value of α. The results obtained with magnesium oxalate ($s_0 = 0{\cdot}00307$) in presence of magnesium

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With a view to get further evidence concerning the solubility effects in the system bi-bivalent salt + bivalent common ion, the solubilities of several salts have been investigated. For this purpose, the succinates and malonates of the alkaline-earth metals afford a suitable range of concentrations. The solubilities of the various salts considered, expressed in gram-molecules per 1000 grams of water, varied between 0·016 and 0·082 weight molar, whilst the total salt concentration did not exceed 0·1 weight molar, except in the case of calcium succinate as saturating salt, with which a maximum of about 0·3 weight molar was reached.

Experimental.

The saturating salts were prepared from pure reagents by precipitation, thorough washing, and drying at the temperature requisite to give the anhydrous salt. Sodium and magnesium succinates were obtained by crystallisation from neutralised succinic acid solutions and were recrystallised several times. Analysis confirmed the purity of the salts thus obtained.

The solubility determinations were carried out in 100 c.c. Jena conical flasks, closed with rubber stoppers and provided with rubber caps. Excess of the saturating salt and a weighed quantity of the other salt were added to a known weight of water in the flask, and the mixture was rotated in a thermostat kept at 25° ± 0·1° until equilibrium had been reached (about 30 hours). The solution, after standing in the thermostat for an hour, was filtered upward by suction through a small filter paper into a weighed flask, which was also in the thermostat. After weighing, the solution was carefully washed out into a beaker and the solubility was obtained by determining gravimetrically the amount of the metallic radical of the saturating salt. Barium was estimated in most cases as sulphate, but in presence of calcium, Browning's method (*Amer. J. Sci.*, 1892, [iii], **43**, 314), depending on the difference in solubility of the nitrates in amyl alcohol, was employed. Calcium was precipitated as oxalate and weighed as sulphate, the precipitation, in presence of magnesium, being carried out twice. Strontium was precipitated as carbonate and weighed as sulphate. In the case of strontium malonate + strontium chloride, the chloride in the solution was determined gravimetrically as silver chloride, and the amount of strontium as malonate was determined by subtraction of

the strontium present as chloride from the total strontium. Independent solubility determinations gave results agreeing within 0·5%.

The results are shown in Table I, s being the solubility, expressed in gram-molecules per 1000 grams of water, corresponding to the weight-molar concentration, c, of added salt; s_0 is the solubility

TABLE I.

s.	c.	s.	c.	s.	c.
Ba succ. + Na succ. $s_0 = 0{\cdot}01570$.		Sr mal. + $SrCl_2$. $s_0 = 0{\cdot}03050$.		Ba succ. + Mg succ. $s_0 = 0{\cdot}01570$.	
0·01307	0·00798	0·02523	0·01828	0·01397	0·00770
0·01154	0·01575	0·02349	0·03103	0·01294	0·01538
0·00987	0·03149	0·02019	0·06149	0·01155	0·03074
0·00913	0·04726			0·01065	0·04620
				0·01024	0·06149
Sr succ. + Na succ. $s_0 = 0{\cdot}02013$.		Ca succ. + Na succ. $s_0 = 0{\cdot}08252$.		Ba succ. + Ca succ. $s_0 = 0{\cdot}01570$.	
0·01740	0·00938	0·08013	0·00826	0·01383	0·00798
0·01535	0·01875	0·07103	0·0506	0·01275	0·01597
0·01322	0·03751	0·06495	0·1014	0·01155	0·03193
0·01221	0·05582	0·06138	0·1526		
0·01143	0·07457	0·05759	0·2560		

Calcium succinate + Magnesium succinate. $s_0 = 0{\cdot}08252$.

s	0·07769	0·07474	0·07340	0·07173	0·07087
c	0·04121	0·06179	0·08230	0·1231	0·1631

of the saturating salt in pure water. The solubility effects, however, can be more easily compared by means of the ratios s/s_0 and c/s_0, which express respectively the concentrations of the saturating salt and of the added salt in terms of the solubility of the former in pure water. These ratios correspond to the terms "fractional solubility" and "fractional concentration" employed by Harkins (*J. Amer. Chem. Soc.*, 1911, **33**, 1851). In Figs. 1 and 2, the values of s/s_0 are plotted against the values of c/s_0, for the addition respectively of uni-bivalent and bi-bivalent salt. For comparison, a typical curve for the system uni-univalent salt + univalent common ion (silver propionate + sodium propionate, Arrhenius, *Z. physikal. Chem.*, 1899, **31**, 225) is also shown (dotted curve).

The curves all lie considerably above the curve for the uni-univalent salt, and for any one saturating salt the curve of Fig. 2 lies above that of Fig. 1. Moreover, for one type of added salt, the curves all lie in the order of the solubility of the saturating salt in pure water, the curve taking a higher position the greater the solubility; this order was found to hold by Harkins (*loc. cit.*) for the salts investigated by him. The lowering effects of calcium and magnesium succinates on the solubility of barium succinate are almost equal, the crosses on curve 2 (Fig. 2) denoting addition of calcium succinate.

Noyes (*J. Amer. Chem. Soc.*, **1924, 46**, 1080, 1098), in his critical presentation of the interionic attraction theory of ionised solutes as put forward by Milner (*Phil. Mag.*, 1912, [vi], **23**, 551; 1913, **25**, 742) and by Debye and Hückel (*Physikal. Z.*, 1923, **24**, 185), uses some of the existing data on the solubility of salts in salt solutions in order to test the validity of the theory. He finds that the solubility effects should be given by an equation, which takes the follow-

FIG. 1.

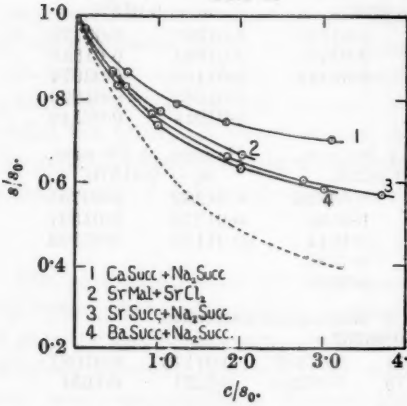
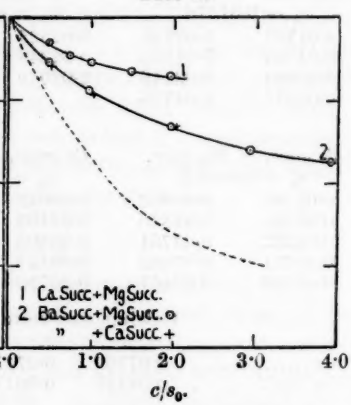


FIG. 2.



ing form for bi-bivalent saturating salts, s_0, s, and c being the concentration terms hitherto employed in this paper,

$$\tfrac{1}{8}\log\frac{s(s+c)}{s_0^2} = \alpha(\sqrt{\Sigma c'\nu^2} - \sqrt{8s_0}),$$

where α has the theoretical value of 0·357 for dilute solutions at 25°. $\Sigma c'\nu^2$ denotes the summation of ion concentration (c') × square of valence of ion (ν^2) for all the ions present, half this quantity representing the " ionic strength " as defined by Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1140). In Table II are shown the values of the coefficient for the two least soluble salts, barium succinate and strontium succinate, calculated from the solubility data in Table I. The values for the system calcium sulphate + magnesium sulphate calculated from the data quoted in Noyes's paper are also shown.

The values in each column are arranged in order of increasing total salt concentration, and it will be seen that in this order α in most cases decreases, reaching a value of about 0·15 at ionic strengths between 0·2 and 0·45 molar. The data for the case of calcium succinate as saturating salt, a salt about four times as soluble as any of the saturating salts in Table II, give even smaller values of α, about 0·09 in the most concentrated solutions. Whilst

TABLE II.

Values of α.

"Ionic strength." $\frac{1}{2}\Sigma c'\nu^2$.	Ba succ. + Mg succ. $s_0=0{\cdot}01570$.	Ba succ. + Ca succ. $s_0=0{\cdot}01570$.	Ba succ. + Na succ. $s_0=0{\cdot}01570$.	Sr succ. + Na succ. $s_0=0{\cdot}02013$.	$CaSO_4$ + $MgSO_4$. $s_0=0{\cdot}01517$.
0·08	0·181	0·173	0·165	0·186	0·201
to	0·177	0·172	0·171	0·166	0·196
0·20	0·164	0·164	0·168	0·158	0·181
0·20	0·153		0·165	0·152	0·169
to					
0·45	0·147			0·145	0·150

the values of α in the first three rows of the table are constant to within about 10%, they are still somewhat smaller than the value 0·238, which Noyes finds to satisfy the experimental facts up to ionic strengths of 0·1*M* in the case of the three salts of higher valence type quoted by him. The differences in the values of α from one another are greater than those which could be due to experimental error in the value of the solubility. An error in the latter as great as 1% (the actual maximum error was about 0·5%) makes a difference of about 5% in the values of α.

Although α increases with decreasing salt concentration, extrapolation from the graph obtained by plotting concentration against the corresponding values of α does not show any tendency for α to reach a value as high as 0·357, even at very small concentrations. In order, therefore, to obtain data at much smaller concentrations than those employed so far in this paper, some experiments were carried out on the solubility of barium and magnesium oxalates in presence of barium chloride and magnesium sulphate respectively. It was hoped that the results of these experiments would give an indication of the value of the "constant" α in Noyes's equation at these much smaller concentrations (about 0·003 to 0·0006 weight-molar), for which the equation ought to hold more closely than in the cases already dealt with. The solubility was determined in each case by titration of the amount of oxalate present in about 200 g. of solution with carefully standardised permanganate solution of such a strength that from 30—60 c.c. were used up in the titration.

From these results, no consistent value for α was obtained in the case of barium oxalate. At small concentrations corresponding to the solubility of barium oxalate, a small error in the experimentally obtained value of the solubility becomes highly magnified in the calculation of α, which may consequently vary enormously. With the more soluble magnesium salt, the influence of an experimental error is not so marked, an error of 1·0% in the solubility causing an error of about 5% in the value of α. The results obtained with magnesium oxalate ($s_0 = 0{\cdot}00307$) in presence of magnesium

sulphate are as follow, the values of α being calculated from Noyes's equation :

s.	*c.*	*a.*
0·00235	0·00272	0·285
0·00215	0·00491	0·320

These values of α are much nearer the theoretical value of 0·357, and the agreement between the two values is fairly good, as the experimental error here corresponded with an error of about 5% in the value of α.

Summary.

(1) The solubility has been determined at 25° of some bi-bivalent salts, *viz.*, succinates and malonates of calcium, strontium, and barium, in pure water and in solutions containing varying concentrations of a common ion. Curves are given which show that the solubility is in every case greater than would be predicted by the solubility product rule, and that the divergence is more marked the greater the solubility of the salt considered, and greater for an added bi-bivalent salt than for an added uni-bivalent salt.

(2) The solubility data have been examined from the point of view of the interionic attraction theory of ionised solutes as developed by Debye and Hückel and especially, from the solubility point of view, by Noyes. The results obtained in this paper are in good qualitative agreement with this theory and, in the case of the very sparingly soluble magnesium oxalate, a fair quantitative agreement is obtained.

In conclusion, I wish to thank Professor Sir James Walker for the interest taken in the progress of this work.

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X.—*Organic Compounds of Arsenic. Part II. Derivatives of the Arsenic Analogue of Carbazole.*

By JOHN ALFRED AESCHLIMANN, NORMAN DEMPSTER LEES, NIAL PATRICK MCCLELAND, and GEORGE NORMAN NICKLIN.

TURNER and BURY have shown (J., 1923, **123**, 2489) that the closure of five-membered arsenic rings of the type *As*-methyldihydroarsindole can be accomplished without difficulty, and two of us have found (J., 1924, **125**, 2025) that the same applies to certain five-membered rings containing three atoms of carbon, one atom of oxygen, and one of arsenic.

It is now shown that the five-membered arsenic ring of analogues of carbazole can be closed with similar ease and it is hoped to give in a future communication an account of the formation of arsenic analogues of indoxyl and related substances.

o-Aminodiphenyl, subjected to the Bart reaction, yields *diphenylyl-o-arsinic acid* (I), and this is converted by warm concentrated sulphuric acid into oo′-*diphenylylenearsinic acid* (II).

(I.)

(II.)

Similarly, diphenylyl-*o*-arsenious chloride, on distillation in a vacuum, is converted into oo′-*diphenylylenearsenious chloride*. Various other derivatives of *oo*′-diphenylylenearsine have been prepared, but the parent substance could not be isolated owing to the readiness with which it is oxidised in the air.

The derivatives are all beautifully crystalline, colourless with the exception of the *iodide*, and non-fluorescent. The melting point is usually about 100° higher than that of the corresponding diphenyl derivative.

Experimental.

o-*Aminodiphenyl*.—Hirsch's method for the preparation of this base (*Ber.*, 1892, **25**, 1973) was modified in that the diazoaminobenzene was prepared as a separate operation, whereby the volume of solvent was much reduced and the tedious drying over potash obviated. Further, since it was not necessary to isolate *p*-aminodiphenyl, the separation of the required base from the other products of the reaction was considerably simplified.

Diazoaminobenzene (150 g.) is covered with 400 g. of aniline (both thoroughly dry) in a large distilling flask, and heated until (at about 150°) a brisk evolution of nitrogen begins; after which the reaction should proceed smoothly to completion, the temperature slowly rising to 180°. Care is necessary not to overheat the mixture, as the reaction may then get out of control. After removal of the aniline, the residue is distilled to about 250° (20 mm.) or until the distillate is very much coloured. The oily distillate is treated with warm dilute sulphuric acid (60 g. in 1 litre for 100 g. of the oil), the residue (diphenylamine and *p*-aminodiphenyl sulphate) removed, and the solution concentrated, almost to dryness. The sulphate of *o*-aminodiphenyl crystallises, while most of the aminoazobenzene sulphate remains in the mother-liquors. The base is obtained from the sulphate in the usual manner and distilled in a vacuum (yield about 25 g.). For further

purification, crystallisation of the hydrochloride from concentrated hydrochloric acid by cooling a saturated solution to $-10°$ is recommended.

Diphenylyl-o-arsinic Acid (I).—Sodium arsenite is coupled with diazotised *o*-aminodiphenyl in alkaline solution at 50—60° in presence of a cupric salt. The acid crystallises from boiling water in bristle-like needles, m. p. 205°. Yield about 60% (Found : C = 51·7; H = 4·1. $C_{12}H_9O_3As$ requires C = 51·8; H = 4·0%).

Diphenylyl-o-arsenious chloride, obtained by the reduction of the above dissolved in warm concentrated hydrochloric acid, by sulphur dioxide in presence of an iodide, is a heavy oil, soluble in chloroform, insoluble in water. On distillation in a vacuum, it loses hydrogen chloride and yields *oo'*-diphenylylenearsenious chloride.

Diphenylyl-o-arsenious oxide, obtained by the action of alcoholic potash on the above, is an amorphous substance with no definite melting point.

oo'-Diphenylylenearsinic Acid (II).—A solution of diphenylyl-*o*-arsinic acid in concentrated sulphuric acid is warmed on the water-bath for a few minutes and poured into water.

oo'-Diphenylylenearsinic acid can be crystallised from very much boiling water, m. p. 290° (Found : C = 55·2; H = 3·5. $C_{12}H_9O_2As$ requires C = 55·4; H = 3·5%).

oo'-Diphenylylenearsenious Chloride.—Diphenylylenearsinic acid is suspended in concentrated hydrochloric acid, an equal volume of chloroform added, and sulphur dioxide and hydrogen chloride are passed in through a wide delivery tube opening under the surface of the chloroform. After some minutes, a little potassium iodide is added and the reduction carried on under reflux on a water-bath, when diphenylylenearsenious chloride passes into the chloroform layer. It is recrystallised from benzene.

oo'-Diphenylylenearsenious chloride crystallises with remarkable readiness, in colourless plates, m. p. 161°, b. p. about 230°/25 mm., readily soluble in chloroform or carbon tetrachloride, less soluble in benzene or alcohol (Found : Cl = 13·3. $C_{12}H_8ClAs$ requires Cl = 13·5%).

Diphenylylenearsenious Iodide.—A suspension of diphenylylenearsinic acid in 10% sulphuric acid is saturated with sulphur dioxide at 60°, and a strong solution of potassium iodide added. After further reduction for an hour, the solid is removed and taken up in benzene; the solution is dried, filtered, and evaporated to small bulk. The *iodide* is then precipitated with alcohol. It forms very beautiful, golden plates, m. p. 166°, soluble in benzene or chloroform, practically insoluble in alcohol.

oo'-*Diphenylylenearsenious oxide*, obtained by the action of warm alcoholic potash on the chloride, or of concentrated aqueous ammonia on the iodide, forms white crystals, m. p. 178°, readily soluble in organic solvents (Found : C = 61·4 ; H = 3·4. $C_{24}H_{16}OAs_2$ requires C = 61·3 ; H = 3·4%). From alcohol it crystallises in needles, m. p. 117°, containing alcohol of crystallisation.

oo'-*Diphenylylenearsenious Cyanide.*—The oxide is dissolved in the least quantity of cold chloroform or of absolute alcohol and treated with anhydrous hydrocyanic acid (⅓ vol.). The product is crystallised from warm absolute alcohol to which a little anhydrous hydrocyanic acid is added as the temperature falls. The cyanide forms long, silky needles, m. p. 178° (like the oxide), soluble in the usual organic solvents (Found : C = 61·5 ; H = 3·1 ; N = 5·5. $C_{13}H_8NAs$ requires C = 61·7 ; H = 3·2 ; N = 5·6%).

Attempts to Prepare oo'-*Diphenylylenearsine.*—To diphenylylenearsinic acid mixed with amalgamated zinc, hydrochloric acid was added and the whole covered with a layer of ether, the air in the flask being replaced by hydrogen. After some days, the clear ethereal layer became cloudy after a short exposure to the air, indicating the presence of the arsine, which could not, however, be isolated. The solution was colourless and non-fluorescent.

Diphenylylenemethylarsine.—By the action of magnesium methyl iodide on diphenylylenearsenious iodide suspended in ether, the yellow colour of the latter was discharged. On working up the product in the usual way, a substance was obtained which crystallised from alcohol in large, transparent prisms, m. p. 46°. It was probably the arsine required, but analytical results were not very satisfactory even after several crystallisations (Found : C = 65·0, 65·1 ; H = 4·4, 4·4. $C_{13}H_{11}As$ requires C = 64·5 ; H = 4·5%). The substance had a pleasant orange-like smell.

Diphenylylenedimethylarsonium iodide, obtained by heating the above with methyl iodide, forms needles, m. p. 190°, soluble in alcohol, insoluble in ether. The iodine is ionic and may be determined by titration with silver nitrate (Found : I = 33·3. $C_{14}H_{14}IAs$ requires I = 33·1%). Methylcarbazole does not combine with methyl iodide.

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[*Received, October 16th*, 1924.]

XI.—*Synthesis of Arachidic Acid and some Long-chain Compounds.*

By Neil K. Adam and Joseph W. W. Dyer.

The melting points of methyl and ethyl arachidates, and eicosyl alcohol, recorded in the literature are several degrees higher than those proper to compounds of their length of chain in the respective series. The regular rise of melting point in the even series of long-chain compounds is more than a mere empirical relationship, since one of us showed (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 528) that from this rise, and other regularities, a crystal structure could be predicted which has since been shown by *X*-ray methods to be correct (Muller and Shearer, J., 1923, **123**, 2043, 3152, 3156). Having synthesised arachidic acid from stearic acid by means of malonic ester, we find that the melting points of these derivatives are as follows. Ethyl arachidate, 41·5° to 42·5°; methyl arachidate, 46° to 47°; eicosyl alcohol, 65° to 65·5°. Previously recorded values are; ethyl ester, 49° (Schweizer, *Arch. Pharm.*, 1884, **222**, 768), 50° (Gossmann, *Annalen*, 1854, **89**, 10); methyl ester, 54·5° (Haller, *Compt. rend.*, 1907, **144**, 598); 53° (Schweizer, *loc. cit.*); alcohol, 71° (Haller, *loc. cit.*). Our values are nearly the mean between the melting points of the compounds in the 18- and 22-carbon series; the older ones are in some cases higher than those in the 22-carbon series. The melting point of arachidic acid itself is 75°, in agreement with previous results and with the position in the series.

The synthesis from ethyl stearate gave a 41% overall yield of pure arachidic acid, and appears to be much the easiest method of obtaining compounds of the C_{20} series pure.

We record also a modification of the Bouveault and Blanc reduction, convenient for long-chain compounds; and new preparations of eicosyl acetate, eicosylamine hydrochloride, eicosylcarbamide, acetohexadecyl- and aceto-octadecyl-amides, dioctadecylmalonic acid, and dioctadecylacetic acid.

Experimental.

Reduction of Long-chain Esters with Sodium and Alcohol.—The higher ethyl esters are troublesome in the ordinary process owing to their small solubility in alcohol. Addition of a large bulk of light petroleum, and substitution of wire or dust for the lumps of sodium, give good yields of the alcohol.

Octadecyl Alcohol.—Well-dried ethyl stearate (150 g.), dissolved in 1200 c.c. of light petroleum and 150 c.c. of absolute alcohol,

was added during ½ hour to sodium wire (72 g.) covered with a little light petroleum to prevent oxidation, at about 80°; heating was continued for 6 hours with occasional shaking. The solvents were distilled off, the residual solid was treated with hot brine, and, after filtration, the product was dried and extracted with ether. The ether was evaporated, and the residue distilled at 12 mm. pressure (yield 68·5%).

For quantities less than 20 g. of ester, the process was modified by using sodium pulverised under xylene, and gave similar yields.

Eicosyl alcohol, from 4·82 g. of ethyl arachidate, was obtained in 70% yield. It was not distilled, but crystallised to constant m. p. (65—65·5°) from 90% alcohol.

Eicosyl acetate, prepared by dissolving the alcohol in glacial acetic acid and passing hydrogen chloride, was crystallised from aqueous acetone; m. p. 39·5—40·5° (Found: C = 77·54; H = 13·04. Calc., C = 77·49; H = 13·05%).

Preparation of Iodides and of Derivatives of Malonic Acid.—Passing hydrogen iodide into the molten alcohols (see Krafft, *Ber.*, 1886, **19**, 2984) gave quantitative yields of the iodides, the gas being practically completely absorbed until the reaction was complete.

The iodide, washed in ethereal solution, was heated with the theoretical amount of sodium and ethyl malonate, in absolute alcohol. The mixture became neutral and gave ethyl mono-octadecylmalonate after 2 hours' boiling and standing over-night. Hydrolysis with strong aqueous potash was nearly instantaneous. The calcium salt was prepared and extracted with alcohol and ether, and the malonic acid liberated in 70% yield (calculated on the iodide used) by rubbing the purified calcium salt with hydrochloric acid in presence of a little ether, which promotes wetting.

Ethyl dioctadecylmalonate could not be prepared in one operation, but was obtained by heating, for 6 hours, 12·2 g. of the crude mono-octadecylmalonic ester with 0·682 g. of sodium, 11·5 g. of octadecyl iodide, and 30 c.c. of absolute alcohol, a little dry ether being added to obtain a homogeneous liquid. After 48 hours' standing, the mixture was neutral. The ester was hydrolysed by heating on the water-bath with alcoholic potash for 10 hours; the *dioctadecylmalonic acid* was purified by means of the calcium salt, as before, and recrystallisation from glacial acetic acid. M. p. 93·5—94° [Found: C = 76·88; H = 12·33. $(C_{18}H_{37})_2C(CO_2H)_2$ requires C = 76·89; H = 12·57%].

Dioctadecylacetic Acid.—Heating dioctadecylmalonic acid at 160° left a residue, m. p. 80—82°; this was raised to 81—82° by crystallisation from acetic acid [Found: C = 80·63; H = 13·59. $(C_{18}H_{37})_2CH{\cdot}CO_2H$ requires C = 80·76; H = 13·56%].

Guthzeit (*Annalen*, 1881, **206**, 362) describes dicetylmalonic acid (m. p. 86—87°) and dicetylacetic acid (m. p. 69—70°); his work has been criticised by Krafft, since the cetyl alcohol used was not pure. If the crystal structure of these compounds is generally the same as that of the simple fatty acids, with the long chains packed side by side and the molecules arranged in pairs of layers, the polar groups of one layer of the pair being next to the polar groups of the other layer, we should expect the difference of two carbon atoms to make a difference of about 3° in the m. p.'s of the dialkylmalonic acids and of about 6° in those of the dialkylacetic acids, which would indicate for the pure dihexadecylmalonic acid m. p. about 91°, and for dihexadecylacetic acid, m. p. about 75°.

Arachidic Acid and its Esters.—The arachidic acid obtained by heating the monooctadecylmalonic acid distilled at 203—205° (uncorr.)/1 mm., and crystallised in leaflets from light petroleum; m. p. 75—75·5°. Titration in alcoholic solution with soda gave the molecular weight 313 (theory 312·3) (Found: C = 76·73; H = 12·96. Calc., C = 76·85; H = 12·90%).

Methyl arachidate was prepared by passing hydrogen chloride into a solution of the acid in pure methyl alcohol, and recrystallising from alcohol. M. p. unchanged on recrystallisation, 46—47° (Found: C = 76·96; H = 12·98. Calc., C = 76·85; H = 12·90%).

Ethyl arachidate, prepared similarly, and crystallised to constant melting point, melted at 41·5—42·5°.

Preparation of Long-chain Amides.—Fileti and Ponzio's method of adding a solution of the acid chloride in ether to aqueous ammonia (*Gazzetta*, 1893, **23**, 391) gives much better results than methods in which the ether is omitted. These frequently give a product with a melting point 10 degrees too low, which probably consists largely of ammonium salt. Using ether as solvent for the chloride, large quantities of the amide may be prepared, the chloride being added very rapidly, and the product is practically pure without crystallisation. The ether is almost entirely driven off by the heat of reaction, and appears to act as a very efficient cooling agent. The aqueous ammonia may be at room temperature.

Arachidamide, m. p. 109°, and the nitrile, m. p. 49·5°, were prepared by the usual methods from the acid.

Eicosylamine hydrochloride was prepared by a modification of Krafft's method (*Ber.*, 1889, **22**, 812) for hexadecylamine. The nitrile (9·7 g.) in 150 c.c. of absolute alcohol was boiled under reflux, 15 g. of sodium being added during 1 hour. The mixture was poured warm into dilute hydrochloric acid, heated with 250 c.c. of absolute alcohol, filtered from any inorganic chlorides, diluted to about 85% alcohol, and cooled. The solution deposited 8·5 g.

of pure eicosylamine hydrochloride, 1 g. more being obtained on concentrating the mother-liquors. For analysis, the chlorine was precipitated with alcoholic silver nitrate (Found: Cl = 10·66. $C_{20}H_{43}N$,HCl requires Cl = 10·64%).

Eicosylcarbamide was easily prepared by evaporating the preceding compound to dryness with excess of potassium cyanate and recrystallising from alcohol. M. p. 111·5° (corr.) (Found: C = 73·98; H = 13·13; N = 8·25. $C_{20}H_{41}$·NH·CO·NH_2 requires C = 74·00; H = 13·04; N = 8·25%).

Monomolecular films of all the compounds of the C_{20} series were examined according to the methods described in previous papers (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 452, 516) and were found to have the properties expected for their respective series and the C_{20} chain, within experimental error; a fact which confirms their identity.

Aceto-octadecylamide.—Octadecylamine hydrochloride (1·4 g.), prepared in the same manner as eicosylamine hydrochloride, was distilled with quicklime, the distillate warmed with acetic anhydride a few minutes, and the product crystallised from acetic acid with the aid of charcoal; m. p., unchanged by further crystallisation, 79·5—80° (yield 66%). The action of acetyl chloride on the amine gave a very poor yield of the desired substance (Found: C = 77·23; H = 13·4; N = 4·75. $C_{18}H_{37}$·NH·CO·CH_3 requires C = 77·09; H = 13·2; N = 4·50%).

Acetohexadecylamide was similarly prepared, and crystallised from acetic acid and acetone to constant melting point (Found: C = 76·46; H = 13·35. $C_{16}H_{33}$·NH·CO·CH_3 requires C = 76·69; H = 13·22%). In the monomolecular films, the acetamides showed a characteristic behaviour, described in another paper, which indicated that the compounds were members of the same homologous series, and differed by two CH_2 groups.

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XII.—*The Adsorption of Catalytically Poisonous Metals by Platinum. Part I. The Adsorption of Lead and Mercury.*

By EDWARD BRADFORD MAXTED.

MEASUREMENTS have been described (J., 1921, **119**, 225; 1922, **121**, 1760) relating to the inhibitive influence of salts of certain metals on the hydrogenation of unsaturated substances and on the decomposition of hydrogen peroxide. In each case it appeared

probable on first principles that adsorption of the metallic salt, or rather of the catalytically poisonous ion, by the catalyst took place; but, since the degree of adsorption was unknown, the inhibitive effect of the poison, measured by the depression in the activity of the catalyst, could only be plotted against the initial bulk concentration of the inhibitant in the reacting system, in place of—as would have been more logical—its actual concentration on the surface of the catalyst itself. Accordingly, the present work was carried out with the object of obtaining data relative to the variation of this adsorbed concentration with the bulk concentration of the inhibitant. The present paper deals with the adsorption of lead and of mercury by finely divided platinum.

EXPERIMENTAL.

An aqueous suspension of platinic oxide was reduced with hydrogen, the precipitated metal washed several times with hot distilled water, and ground thoroughly in an agate mortar in presence of a little water. This method of preparing the platinum was found preferable to the reduction of a platinum salt with formaldehyde or other reducing agent on account of the difficulty, in such cases, of freeing the preparation from adsorbed impurities.

In carrying out each adsorption experiment, 1 c.c. of a stock suspension of platinum, containing 4·48 mg. of platinum per c.c., was added to a system containing a known quantity of a lead or mercury salt dissolved in 9 c.c. of water, the mixture was thoroughly agitated, kept over-night at 20°, and an appropriate portion of the clear liquid taken for analysis.

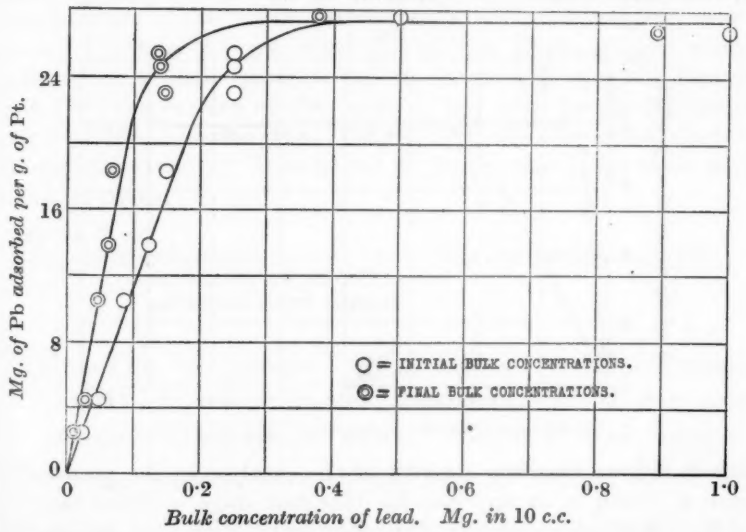
The concentration of lead or mercury salt remaining unadsorbed was determined by observing the toxic effect of a known fraction of the solution on the activity of a standard catalyst for the decomposition of hydrogen peroxide, for which reaction the inhibitive effect of various known concentrations of the lead and mercury salts in question had previously been mapped for the catalysts employed. It was thus possible to estimate with considerable accuracy small fractions of a milligram of lead or of mercury.

Adsorption of Lead.—An aqueous solution of lead acetate, usually containing 0·1 mg. of lead per c.c., was employed; for certain experiments, solutions of one-tenth and ten times this strength, respectively, were used. Preliminary experiments with potassium acetate showed that the acetate ion is, at any rate in the concentrations employed, without appreciable toxic action on platinum for the decomposition of hydrogen peroxide.

The result of a series of adsorption experiments, in each case with 4·48 mg. of platinum, is shown graphically in Fig. 1. It will

be seen, on plotting the weight of lead adsorbed against its initial concentration, that a linear relationship exists between these two quantities up to a stage at which the platinum surface apparently approaches saturation; and further adsorption, from this stage onwards, takes place only to a slight degree on increasing the initial bulk concentration of the lead salt. The two graphs in the figure were obtained by plotting the weight of lead adsorbed per gram of platinum, first, against the initial bulk concentration and, secondly, against the final bulk concentration of the unadsorbed lead in the system. This result is analogous to those obtained by Euler and Hedelius (*Arkiv Kem.*, 1920, **7**, 31) for the adsorption of a silver

FIG. 1.



salt by silver and gold, for which also an initially linear adsorption graph was obtained.

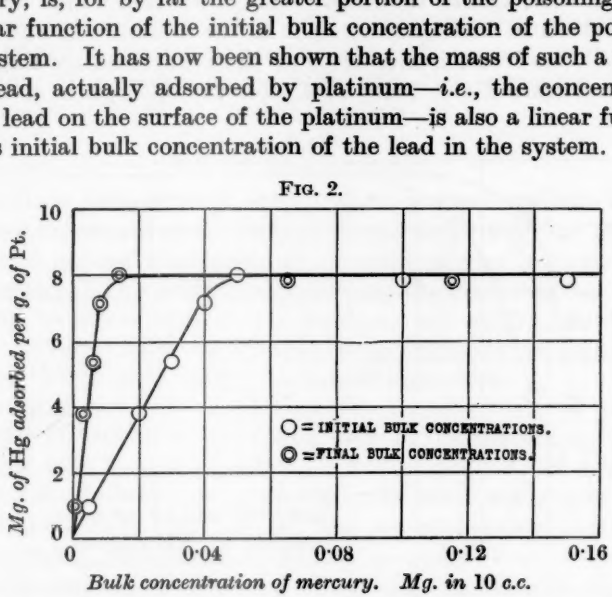
Adsorption of Mercury.—A dilute solution of mercuric chloride was employed, the other conditions being similar to those adopted for lead.

Fig. 2 gives the results of a series of adsorption experiments, carried out, as before, with 4·48 mg. of finely divided platinum. For initial concentrations of mercury below that corresponding with the saturation of the platinum, the adsorption of mercury is practically complete; and the very small concentration of mercury remaining after adsorption could be estimated with the required degree of accuracy only by virtue of the method of analysis employed (see above).

The linear nature of the adsorption graph for mercury, and the abrupt break in this graph immediately before the saturation point, are very striking.

The form of the adsorption graph both for lead and for mercury, on platinum, may be compared with that of the poisoning curve. It has previously been shown (*loc. cit.*) that the decrease in the activity of a platinum catalyst, caused by a poison such as lead or mercury, is, for by far the greater portion of the poisoning curve, a linear function of the initial bulk concentration of the poison in the system. It has now been shown that the mass of such a poison, *e.g.*, lead, actually adsorbed by platinum—*i.e.*, the concentration of the lead on the surface of the platinum—is also a linear function of this initial bulk concentration of the lead in the system. From

FIG. 2.



this it follows that the activity of the catalyst in the presence of such a poison is, at any rate for this first stage, a linear function of the actual concentration of the lead on the surface of the catalyst.

This result was to be expected on theoretical grounds, since the free valency forces on the surface lattice of the platinum will, if they are saturated by a difficultly evaporable poison, such as lead, no longer be free for the adsorption of, or association with, a potentially reactive system, it being presumed that catalysis normally takes place by reason of such association. Therefore, since each atom of lead thus obstructively adsorbed will cause a given number (one or more) of such valency bonds to become no longer active for normal catalysis, the poisoning of this catalytic surface should be a linear function of the concentration of the poison on the surface, a result which has just been obtained experimentally.

From Fig. 1 it is seen that the linear relationship between the concentration of the lead on the catalyst and its bulk concentration

in the solution ceases, as is necessarily the case, in the region bordering on the saturation of the surface of the platinum by the lead, in which region the initially linear adsorption graph becomes more or less abruptly converted into a line parallel with the bulk concentration axis and denoting saturation.

In the poisoning graphs previously obtained for such cases, the initial linear portion—during which the activity of the catalyst is a linear function of the initial bulk concentration of the poison in the system—is also followed, in a very similar way, by a break, followed in turn by a far less steep portion, which, like the adsorption curve, becomes approximately parallel with the bulk concentration axis. It appears of great interest to ascertain whether the break in the poisoning graph, obtained by plotting activity against bulk concentration of the poison, occurs at the region of incipient saturation. If this is the case, then the activity of the catalyst would seem to be linearly proportional to the actual concentration of poison on the surface of the catalyst, not only during the major portion of the poisoning graph, but also up to the complete extinction of catalytic activity. It is hoped to discuss this point more fully in a later paper.

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XIII.—*The Explosion of Acetylene and Nitrogen. Part IV. Spectra of Explosions of Gases containing Hydrogen, Carbon, Nitrogen, and Oxygen.*

By WILLIAM EDWARD GARNER and SIDNEY WALTER SAUNDERS.

THE origin of the Swan and cyanogen band spectra has frequently been discussed, and although the former is usually ascribed to free carbon (Watts, *Phil. Mag.*, 1914, [vi], **28**, 117) and the latter to carbon and nitrogen, opinion is not unanimous on these questions. Before 1914, it was believed that the cyanogen bands were due to carbon and nitrogen, but Grotrian and Runge (*Physikal. Z.*, 1914, **15**, 545) reopened the discussion on the origin of this spectrum, and concluded, as a result of their experiments with the electric arc, that the so-called cyanogen spectrum was due to nitrogen alone. This view seems to have been widely accepted, although neither Barratt (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 40), who experimented with flames, nor Hemsalech (*Phil. Mag.*, 1920, [vi], **39**, 241), nor Holst and Oosterhuis (*K. Acad. Amsterdam Proc. Sci.*, 1921, **23**, 1, 727), who suppressed the cyanogen bands by immersing

their nitrogen and argon discharge tubes in liquid oxygen, and so freezing out the cyanogen, have confirmed it. The results obtained in this paper also indicate that the presence of both carbon and nitrogen is essential for the production of the "cyanogen" spectrum.*

It has been found that the nature of the spectrum emitted during explosions of acetylene in oxygen and nitrogen is very largely dependent on the ratio of gram-atoms of carbon to oxygen in the mixture. With low percentages of oxygen, where large quantities of carbon are deposited during the explosion, a continuous spectrum only is obtained. The carbon, being an almost perfect black body, acts as a screen cutting off the radiation emitted from the molecules activated during the explosion. As the ratio of oxygen to acetylene approaches unity, the Swan, CH, and cyanogen bands, and metallic absorption and emission lines appear on the background formed by the continuous spectrum, which simultaneously diminishes in intensity. These band spectra persist into the region where oxygen>carbon, but gradually fade away as the oxygen percentage is increased, until, finally, with a still larger proportion of oxygen, only the line emission and absorption spectrum of the metallic impurities are present.

The Swan and cyanogen spectra appear and disappear together as the oxygen percentage increases. Their disappearance occurs approximately at the concentrations found previously (J., 1924, **125**, 1634) for the disappearance of free carbon and hydrocyanic acid from the final products of the explosion, *viz.*, when the ratio of oxygen to carbon becomes unity. Thus the presence of free carbon in the products of the explosion is essential not only for the production of hydrocyanic acid but also for both the Swan and the cyanogen spectra.

The Swan and cyanogen spectra persist into the region where oxygen is in excess (up to $C : O = 0{\cdot}956$ for mixtures of C_2H_2 and O_2, and $C : O = 0{\cdot}968$ for mixtures of O_2, N_2, and C_2H_2), but this does not invalidate the above conclusion, for the spectrum of the explosion is a record of the radiation emitted throughout the whole of the explosive process and hence includes the radiation emitted before equilibrium is reached.

On the molecular collision view of the propagation of the explosion wave, undecomposed acetylene molecules immediately in front of the wave will be bombarded by swiftly moving molecules of carbon, hydrogen, oxygen, carbon monoxide, etc., from the explosion wave itself. An oxygen molecule, in collision with an acetylene mole-

* Since this paper was written Freundlich and Hochheim (*Z. Physik*, 1924, **26**, 102), in furnace experiments, have shown that elementary carbon is essential for the production of this spectrum.

cule, would be likely to give carbon monoxide but no free carbon, $C_2H_2 + O_2 \longrightarrow 2CO + H_2$, but any other molecule may bring about the change $C_2H_2 \longrightarrow 2C + H_2$. Thus even in the presence of excess of oxygen free carbon may be momentarily formed, and, if the average life of the carbon particles (C_2 possibly) before removal as carbon monoxide is long enough, the Swan spectrum may be emitted. This would explain our results (Table I).

The results of this investigation thus support the view that carbon is necessary for the production of the cyanogen spectrum. That nitrogen also is necessary is evident from the absence of the cyanogen spectrum in the spectra of explosions of acetylene and oxygen alone.

Experimental.

An examination has been made of the spectra from the following series of explosive mixtures : (*a*) pure acetylene, (*b*) acetylene and nitrogen, (*c*) acetylene and oxygen, (*d*) acetylene, oxygen, and nitrogen, (*e*) electrolytic gas, (*f*) carbon monoxide and oxygen, (*g*) coal gas and oxygen.

Apparatus.—A 2-litre phosphor-bronze bomb similar to that described by Wheeler (J., 1918, **113**, 855) was fitted with a cylindrical quartz window, 6 mm. in diameter and 8 mm. thick, placed opposite the collimator tube of a Hilger Constant Deviation Spectrometer.* Ignition of the gaseous mixture was usually accomplished by fusion of a thin iron wire placed across the terminals in the centre of the bomb. In some experiments, the position of firing of the mixture was changed and in others, the iron wire was replaced by platinum.

Preparation of the Gases.—The acetylene, from a cylinder containing the gas compressed in acetone, was washed with water, dried over phosphorus pentoxide, and stored over mercury. It was completely soluble in a solution of ammoniacal cuprous chloride. Oxygen and nitrogen were prepared as described elsewhere (*loc. cit.*). Carbon monoxide, obtained by the action of sulphuric acid on sodium formate, was washed with sodium hydroxide and dried over phosphorus pentoxide. Electrolytic gas was prepared from baryta. The gases were introduced into an evacuated bomb, which had been previously washed out six times with oxygen. This repeated washing was necessary in order to ensure the absence of nitrogen in the first series of experiments. The composition of the gaseous mixture was determined by pressure measurements.

Measurement of Spectra.—Each photograph of the explosion spectrum was bracketed by photographs of a neon–helium lamp, the wave-lengths of the lines in this spectrum being known, and

* A few measurements were made with a quartz spectrometer.

the lines were measured by means of a travelling microscope. The extreme errors of measurement were $\pm$ 1Å. for the band spectra and 0·2 Å. for the metallic lines.

Results.

(a) *Acetylene and Oxygen.*—With pure acetylene, and also acetylene and oxygen mixtures up to 41% of oxygen, a perfectly continuous spectrum was obtained (Table I). With 100% acetylene, the spectrum was rather more brilliant in the red than is the case with the mixture containing 41% of oxygen. The effect of the addition of oxygen on the position of maximum light intensity is to shift this maximum slightly towards the blue end of the spectrum, this being in agreement with Wien's displacement law.

TABLE I.

Oxygen and Acetylene. $P = 1$ atm.

% O_2.	% C_2H_2.	% C_2H_2/% O_2.	Spectrum.
—	100·0 *	—	Continuous with no line or band spectra.
35·22	64·78	1·837	
41·10	58·90	1·433	
49·33	50·67	1·028	Swan and CH bands with faint metallic lines.
49·58	50·42	1·017	
49·69	50·31	1·013	
50·30	49·70	0·988	Swan and CH bands with metallic lines.
51·12	48·88	0·956	
53·14	46·86	0·882	Metallic lines only.
55·50	44·50	0·802†	
59·86	40·14	0·671	
62·91	37·09	0·590†	

* 3·2 atm. † Platinum wire ignition.

As the ratio (column 3) approaches unity, the Swan, "the three," and the CH bands appear on the continuous spectrum. The bands 6191, 5635, 5165, 4737, 4382, 4371, 4365, and 4314 Å. were observed. These bands first appear when the value, $\%C_2H_2/\%O_2$, is between 1·433 and 1·035; the exact value was not found.

It was anticipated that the Swan spectrum would disappear when $\%C_2H_2/\%O_2 < 1$, since at the temperature of explosion, *ca.* 3000°, the equilibrium constant for the reaction $C + H_2O = CO + H_2$ is $K_p = P_{CO}P_{H_2}/P_{H_2O} = 10^5$, and hence practically no free carbon can be present if the gaseous mixture attains equilibrium.

Since the Swan spectrum is considered as being due to free carbon, it was expected that this, together with "the three" and CH bands would disappear when the ratio $\%C_2H_2/\%O_2 < 1$. It was found, however, that these bands persisted even when the acetylene–oxygen mixture had the ratio $\%C_2H_2/\%O_2 = 0{\cdot}956$, although they had all disappeared when the ratio became 0·882.

The cyanogen spectrum was not observed in this series of experiments.

(b) *Acetylene, Nitrogen, and Oxygen.*—When nitrogen was added until the mixture had the composition 82% C_2H_2, 18% N_2, and the mixture was fired under a pressure of about 3 atmospheres, several units per cent. of hydrocyanic acid were obtained and yet the spectrum was still continuous. Since the amount of free carbon could not be reduced sufficiently by the addition of nitrogen alone to enable emission and absorption lines to be obtained, oxygen was added to the mixture until the ratio $\%C_2H_2/\%O_2$ was between 1·1 and 1. This diminished the carbon sufficiently for the Swan, "the three," and the CH bands to be observed, and, in addition, the cyanogen bands, 4216 Å. and 3883 Å. These all persisted when the ratio $\%C_2H_2/\%O_2 = 0{\cdot}968$ (Table II). Further addition

TABLE II.

Oxygen, Nitrogen, and Acetylene. $P = 1$ atm.

% O_2.	% C_2H_2.	% N_2.	% C_2H_2/% O_2.	Spectrum.
—	82·2	17·8	—	Continuous spectrum.
47·98	49·56	2·46	1·035	Swan, CH, cyanogen bands and faint metallic lines.
40·72	41·81	17·47	1·026	
48·65	49·22	2·13	1·012	
49·28	49·99	0·73	1·013	
39·58	40·06	20·36	1·012	
46·72	46·14	7·14	0·988	Swan, CH, cyanogen bands and metallic lines.
45·97	45·28	8·55	0·985	
39·96	39·11	20·93	0·977*	
42·92	41·49	15·60	0·968	
41·59	40·28	18·13	0·968	Metallic lines only.
43·13	39·45	17·42	0·915	
45·29	37·36	17·35	0·825	
51·66	39·79	8·55	0·770	
56·04	34·73	9·23	0·620	

* No band spectra.

of oxygen causes the disappearance of these spectra. If Grotrian and Runge's contention be correct, that nitrogen will give rise to the "cyanogen" spectrum if no appreciable amount of oxygen be present, then the above-mentioned disappearance of this spectrum, when $\%C_2H_2/\%O_2 = 0{\cdot}915$, is not easy to explain, for in such a mixture at the temperature of the explosion there can be but little free oxygen.* The disappearance of this spectrum is understandable, however, if it be due to both carbon and nitrogen.

The nature of the spectrum is the same, whatever the position of the iron wire used for igniting the gases; placing the iron wire close to the side of the bomb or directly in front of the quartz window made no difference.

* Approximately 0·001 % of oxygen at 3000° abs.

The only lines present in the spectra of the explosions of hydrogen and oxygen, and carbon monoxide and oxygen, were those due to the metallic impurities present, *e.g.*, sodium, calcium, iron, etc. As would be expected on account of the lower temperature of these flames, the metallic lines were not so numerous as in the acetylene explosions.

Summary.

The spectra emitted during the explosion of mixtures of acetylene, nitrogen, and oxygen have been studied. The results indicate that the cyanogen spectrum is due to both carbon and nitrogen.

The authors wish to express their indebtedness to the Department of Scientific and Industrial Research for a maintenance grant to one of them (S. W. S.) and for an equipment grant towards the cost of apparatus.

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XIV.—*Reactions of Displacement in the Tropic Acid Group. Part I.*

By ALEX. MCKENZIE and ROBERT CAMPBELL STRATHERN.

THE proof of the constitution of α-aminohydratropic acid, $NH_2 \cdot CPhMe \cdot CO_2H$, was afforded by Tiemann and Köhler (*Ber.*, 1881, **14**, 1980) by the synthesis from acetophenonecyanohydrin and alcoholic ammonia. McKenzie and Clough (J., 1912, **101**, 390), in dealing with the Walden inversion, described the resolution of the *r*-acid into its optically active components.

The study of the isomeric β-acid, $NH_2 \cdot CH_2 \cdot CHPh \cdot CO_2H$, has not so far been advanced to the corresponding stage. For one reason, this acid has no particular interest with relationship to the Walden inversion, the amino-group not being directly attached to the asymmetric carbon atom. The identification of the acid has also been attended with some confusion. By the action of aqueous ammonia on β-bromohydratropic acid, Merling (*Annalen*, 1881, **209**, 11) obtained crystals, m. p. 169—170° (compare also Fittig and Wurster, *ibid.*, 1879, **195**, 158). Assuming that the reaction proceeded on the lines

$$CH_2Br \cdot CHPh \cdot CO_2H \longrightarrow NH_2 \cdot CH_2 \cdot CHPh \cdot CO_2H,$$

Merling concluded that he had to deal with β-aminohydratropic acid, and the analytical evidence supported this assumption.

Posner, however, in continuation of his work on the action of hydroxylamine on unsaturated acids, obtained from atropic acid an amino-acid which melted and decomposed at 234° (*Ber.*, 1903, **36**, 4315; *Annalen*, 1912, **389**, 109). All the evidence pointed to this substance being the true β-aminohydratropic acid. Since Posner (*Ber.*, 1905, **38**, 2316) had shown that the action of ammonia on β-bromo-β-phenylpropionic acid leads to the formation not of β-amino-β-phenylpropionic acid but of β-hydroxy-β-phenylpropionamide, he suggested that β-bromohydratropic acid might perhaps exhibit a similar behaviour, and that Merling's product was not the amino-acid at all, but was the isomeric tropamide.

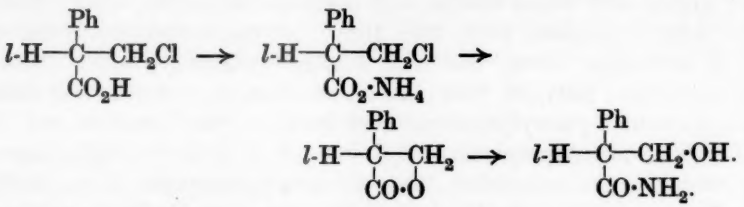
The latter suggestion has been borne out. In the present paper it is shown that *r*-β-chlorohydratropic acid is converted into *r*-tropamide (m. p. 170—171°) by the action of aqueous ammonia. The amide was also prepared directly from ammonia and methyl *dl*-tropate; it has the same melting point, and it possesses the same properties as the compound described by Merling.

We have also examined the action of hydroxylamine on atropic acid, and find that Posner's β-amino-acid is not the sole product, and that the oxime of phenylacetaldehyde is also formed. It is, however, rather curious that the formation of tropic acid by the action of nitrous acid on the amino-acid proceeds in a somewhat irregular manner.

The preparation of *l*-β-chlorohydratropic acid is described, the resolution of the *r*-acid being effected in methyl-alcoholic solution with morphine as the resolving alkaloid. When hydrolysed, the *l*-acid, which has $[\alpha]_D - 122{\cdot}6°$ in benzene, gave a lævorotatory tropic acid with $[\alpha]_D - 58{\cdot}1°$ ($c = 2{\cdot}4348$) in ethyl-alcoholic solution, whereas the value for the optically pure acid is $[\alpha]_D - 72{\cdot}5°$ ($c = 2{\cdot}578$) in the same solvent (McKenzie and Wood, J., 1919, **115**, 828). Although the chlorine is not directly attached to the asymmetric carbon atom, some racemisation had apparently taken place during the substitution of the hydroxy-group for the chlorine.

In the light of recent work in a different field (McKenzie and Roger, J., 1924, **125**, 2148), the action of ammonia on the *l*-chloro-acid was of some interest, and we have therefore examined it for the purpose of finding if optical activity would persist in the transformation into the amide. Experiments showed that a lævorotatory tropamide did actually result. Under the conditions employed, the rotation of the product was less than that of the amide obtained by the direct action of ammonia on ethyl *l*-tropate. This formation of an optically active tropamide has led us to

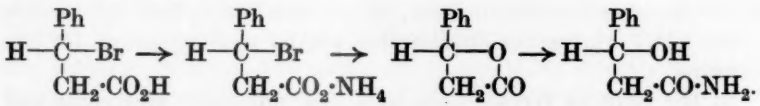
conclude that a β-lactone is produced as an intermediate phase, thus:



Although on those lines the actions do not occur by substitution of groups directly attached to the asymmetric carbon atom, some racemisation accompanied the change. This was not altogether unexpected, since in tropamide we have the phenyl, hydrogen, and carbonyl groups all directly attached to the asymmetric carbon atom, a system which, at any rate in the presence of alcoholic alkali, is particularly prone to racemisation under certain conditions (McKenzie and Smith, J., 1922, **121**, 1348).

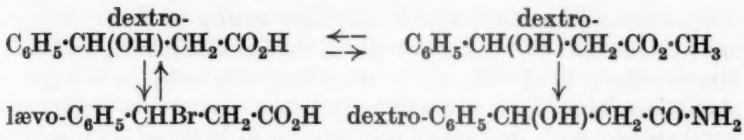
In the field of optical activity, it has been shown by Holmberg (*Arkiv Kem. Min. Geol.*, 1917, **6**, No. 23, pp. 1-33, and earlier papers) that the formation of a β-lactone is a stage in the interconversion of *d*- and *l*-malic acids by the Walden inversion. Moreover, *l*-iodosuccinic acid, when treated with ammoniacal silver nitrate, gives a mixture of fumaric acid and *d*-β-malamic acid, the latter being formed by the action of ammonia on the *d*-malo-lactone (compare Walden and Lutz, *Ber.*, 1897, **30**, 2796; Lutz, *Ber.*, 1902, **35**, 2460, 4369; 1908, **41**, 841).

Reference has already been made to the fact that Posner obtained *r*-β-hydroxy-β-phenylpropionamide by the action of ammonia on *r*-β-bromo-β-phenylpropionic acid. It seems reasonable to suppose that this action proceeds on similar lines to that of ammonia on β-chlorohydratropic acid:



It will be observed that the β-lactone which is suggested as an intermediate phase is isomeric with the one postulated in the scheme with β-chlorohydratropic acid.

Arising from the results recorded in the present paper, and more especially from former work by one of us, it is desirable that Posner's observation should be extended to the optically active β-bromo-β-phenylpropionic acids so as to enable the following scheme to be completed:



(McKenzie and Humphries, J., 1910, **97**, 121; McKenzie and Martin, J., 1913, **103**, 112; McKenzie, Martin, and Rule, J., 1914, **105**, 1583; McKenzie and Smith, J., 1922, **121**, 1348). Owing to the announcement in the current number of the *Proceedings* (1924, p. 77) of a paper by Senter and Ward entitled "Studies on the Walden inversion. Part IX. The influence of the solvent on the sign of the product in the conversion of β-bromo-β-phenylpropionic acids to β-hydroxy-β-phenylpropionamides," we are not, meanwhile, investigating this matter further, so far as the action of ammonia on the optically active β-bromo-β-phenylpropionic acids is concerned. At present, we are engaged on a further study of the action of nitrous acid on *r*-β-aminohydratropic acid, and also propose to undertake the resolution of this acid with the object of examining the resulting optically active acids.

Experimental.

Action of Hydroxylamine on Atropic Acid.—Posner (*Annalen*, 1912, **389**, 112) prepared *r*-β-aminohydratropic acid by heating atropic acid with an alcoholic solution of hydroxylamine for 1 hour. By analogy with his previous work (*Ber.*, 1905, **38**, 2316; compare also McKenzie and Tudhope, J., 1924, **125**, 923), it might be expected that the formation of the amino-acid would be accompanied by that of phenylacetaldoxime. This oxime was isolated as follows.

Hydroxylamine hydrochloride (25 g.) in water (25 c.c.) was added to a solution of sodium (8·5 g.) in ethyl alcohol (280 c.c.), and the precipitated sodium chloride removed. Atropic acid (25 g.), prepared by the dehydration of atrolactinic acid (McKenzie and Wood, *loc. cit.*), was added, and the solution boiled for 1½ hours. Ammonium carbonate was deposited in the condenser tube. After 3 days in the ice-chest, the amino-acid (8 g.) was collected; it was free from the hydroxylamino-acid, since it did not reduce either Fehling's solution or ammoniacal silver nitrate; it melted and decomposed at 222—224° (Posner gives 233°). An additional 0·5 g. was obtained by boiling the filtrate for 2½ hours longer. After distillation of the bulk of the alcohol, an excess of water precipitated 8 g. of crude phenylacetaldoxime, which, crystallised from water several times, gave the pure substance in lustrous needles, m. p. 103—104° (Found: C = 70·9; H = 6·8. Calc., C = 71·1; H = 6·7%). Bouveault and Wahl (*Compt. rend.*, 1902, **134**, 1147) gave m. p. 103°.

r-β-Aminohydratropic acid is sparingly soluble in water, benzene, light petroleum, acetone, chloroform, carbon disulphide, and ether. Posner (*Ber.*, 1903, **36**, 4315) described this acid as α-amino-α-phenylpropionic acid (α-aminohydratropic acid); its solution in hydrochloric acid was acted on by nitrous acid to give an acid, m. p. 89—90°, which was supposed to be atrolactinic acid. Posner was, however, working with small quantities of material, and was misled by the erroneous data of other authors. In a subsequent paper (*Annalen*, *loc. cit.*), the correct constitution of the amino-acid is given. The product, which Posner obtained by the action of nitrous acid, was apparently impure tropic acid. We have repeated this action several times and find that it proceeds by no means smoothly. The gradual addition of potassium nitrite to the solution of the amino-acid in dilute hydrochloric acid caused the deposition of an oil, which was certainly not tropic acid, nor did it appear to be α-*iso*tropic acid, since it showed no signs of solidifying when nucleated with the latter acid. The aqueous solution was separated from the oil and extracted with ether. By crystallising the resulting acid several times from benzene, *r*-tropic acid was isolated in very small yield (0·1 g. of the pure acid, m. p. 116—117°, from 2 g. of β-aminohydratropic acid).

Resolution of r-β-*Chlorohydratropic Acid.*—The solution obtained by boiling 49·5 g. of morphine (1 mol.) in 820 c.c. of methyl alcohol was cooled to 42°, and 30 g. of *r*-β-chlorohydratropic acid (1 mol.; prepared from atropic acid: McKenzie and Wood, *loc. cit.*) were added in one instalment with vigorous stirring. The acid dissolved quickly. When the temperature had fallen to 39°, glassy prisms started to separate. After 18 hours in the ice-chest, 56 g. of solid were deposited. After the evaporation of the methyl alcohol from the filtrate, the acid obtained from the latter gave the following rotation in benzene: $l = 2$, $c = 3{\cdot}924$, $\alpha_D^{14^\circ} + 3{\cdot}71°$, $[\alpha]_D^{14^\circ} + 47{\cdot}3°$, so that the resolution had proceeded markedly after one crystallisation. The further progress is indicated as follows: 56 g. crystallised from 1350 c.c. of methyl alcohol → 35 g., 850 c.c. of alcohol → 19 g., 550 c.c. of alcohol → 13 g., 400 c.c. of alcohol → 9 g., 360 c.c. of alcohol → 6 g. pure morphine *l*-salt. The solution of the crystals in methyl alcohol should be conducted as expeditiously as possible. The progress of the resolution was tested by the polarimetric examination of the acids obtained from the mother-liquors. The morphine salt, which separates in rectangular prisms, was decomposed by dilute sulphuric acid, the solution extracted with ether nine times, and the ethereal extract dried with anhydrous sodium sulphate. The resulting acid (2·1 g.), after drying in a vacuum until constant in weight, gave the following rotation in benzene:

$l = 2$, $c = 3{\cdot}536$, $\alpha_D^{16°} - 8{\cdot}66°$, $[\alpha]_D^{16°} - 122{\cdot}4°$. The acid was crystallised from light petroleum (b. p. 60—80°), and gave a value for the rotatory power agreeing with the above within the limits of experimental error: $l = 2$, $c = 3{\cdot}536$, $\alpha_D^{16°} - 8{\cdot}67°$, $[\alpha]_D^{16°} - 122{\cdot}6°$.

l-β-*Chlorohydratropic acid*, m. p. 62·5—63·5°, separates from light petroleum in rosettes of glassy plates. It is sparingly soluble in light petroleum, and readily so in ether, carbon disulphide, benzene, and ethyl alcohol (Found: Cl = 19·39. $C_9H_9O_2Cl$ requires Cl = 19·24%).

In acetone: $l = 2$, $c = 3{\cdot}2300$, $\alpha_D^{15·5°} - 7{\cdot}46°$, $[\alpha]_D^{15·5°} - 115{\cdot}5°$.

Conversion of l-β-*Chlorohydratropic Acid into* l-*Tropic Acid.*—*N*-Sodium carbonate (11 c.c.) was gradually added (14 mins.) to a boiling solution of the *l*-acid (1 g.) in 20 c.c. of water (reflux). The boiling was continued for 3 hours, the cold solution extracted with ether to remove the styrene present, and the tropic acid obtained by acidification with dilute sulphuric acid and extraction with ether. Yield 0·7 g. In ethyl alcohol: $l = 2$, $c = 2{\cdot}4348$, $\alpha_D^{18·5°} - 2{\cdot}83°$, $[\alpha]_D^{18·5°} - 58{\cdot}1°$.

A similar experiment was carried out with a lævorotatory acid having $[\alpha]_D^{16°} - 100{\cdot}7°$ ($l = 2$, $c = 3{\cdot}5504$) in benzene. The resulting tropic acid (1·9 g.) gave the following value in ethyl alcohol: $l = 2$, $c = 2{\cdot}716$, $\alpha_D^{14°} - 2{\cdot}68°$, $[\alpha]_D^{14°} - 49{\cdot}3°$. After one crystallisation of this product from benzene, the value for the specific rotation was enhanced: in ethyl alcohol, $l = 2$, $c = 2{\cdot}548$, $\alpha_D^{17°} - 3{\cdot}17°$, $[\alpha]_D^{17°} - 62{\cdot}2°$.

Conversion of l-β-*Chlorohydratropic Acid into* l-*Tropamide.*—A solution of the *l*-chloro-acid (0·94 g.) in 60 c.c. of aqueous ammonia (saturated at 0°) was kept for a week in a pressure flask at the ordinary temperature. When the solution was transferred to a crystallising dish, needles began to separate. Yield: 0·3 g.; m. p. 195—199° (Found: N = 8·7. Calc., N = 8·5%). In ethyl alcohol: $l = 2$, $c = 0{\cdot}3472$, $\alpha_D^{17°} - 0{\cdot}38°$.

In another experiment the resulting amide gave in ethyl alcohol: $l = 2$, $c = 0{\cdot}3912$, $\alpha_D^{16°} - 0{\cdot}43°$.

The concentrations employed were necessarily very small, the amide being sparingly soluble in water, ethyl alcohol, acetone, chloroform, benzene, and ethyl acetate.

For the purpose of comparison, the amide was prepared from *l*-tropic acid (obtained by resolution of the *r*-acid with morphine according to McKenzie and Wood) by acting on the ethyl ester with concentrated aqueous ammonia. After crystallisation from acetone, the amide had m. p. 195—197·5°; in ethyl alcohol: $l = 1$, $c = 0{\cdot}377$, $\alpha_D - 0{\cdot}24°$. Since the polarimetric determinations could be made with very dilute solutions only, we have no proof

that we obtained the optically pure *l*-tropamide by this method, more especially since there was always the possibility of partial racemisation having taken place during the action of ammonia on the *l*-ester. But we think it likely that we obtained the amide nearly pure, if not quite so.

l-Tropamide would be expected to undergo racemisation in the presence of a small amount of sodium ethoxide (McKenzie and Smith, J., 1922, **121**, 1348). When 0·5 c.c. of ethyl-alcoholic potash (0·6518*N*) was added to a solution giving $\alpha_D - 0{\cdot}24°$ ($l = 1$), the lævorotation gradually dropped to zero after 30 hours, and *r*-tropamide (m. p. 170—171°) was isolated from the solution.

Formation of r-*Tropamide from* r-*Tropic Acid and* r-β-*Chlorohydratropic Acid.*—*r*-Tropic acid was converted into its methyl ester, from which the amide was prepared by the action of aqueous ammonia.

r-Tropamide, m. p. 170—171°, is sparingly soluble in cold water, ethyl alcohol, acetone, benzene, carbon tetrachloride, and light petroleum (b. p. 60—70°). It separates from water in needles (Found: N = 8·4. $C_9H_{11}O_2N$ requires N = 8·5%).

A solution of *r*-β-chlorohydratropic acid (4 g.) in concentrated aqueous ammonia (65 c.c.) was kept for 18 days in a pressure flask. On pouring into a dish, crystallisation started quickly. The crystals (1·5 g.) were collected and crystallised twice from water, when the pure *r*-tropamide (m. p. 170—171°) was obtained (Found: C = 65·1; H = 6·8. Calc., C = 65·4; H = 6·7%). The melting point was not depressed when this product was mixed with the *r*-tropamide obtained from methyl *dl*-tropate.

One of us (R. C. S.) wishes to thank the Carnegie Trust for the award of a Scholarship which enabled him to take part in the above investigation.

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XV.—*Preparation of Quaternary Hydrocarbons.*

By EDWARD RUSSELL TROTMAN.

IN the course of some investigations in progress in this laboratory, certain quaternary hydrocarbons of the type $(C_6H_5{\cdot}CH_2)_2CR_1R_2$ were required, R_1 and R_2 being different alkyl radicals. No such compounds are known, and indeed very few quaternary hydrocarbons of any kind have been described. The interaction of Grignard reagents and tertiary halogen derivatives, which seemed

to offer a suitable method for their preparation, has already been studied. Gomberg and Cone (*Ber.*, 1906, **39**, 1461, 2975) succeeded in displacing the chlorine atom of triphenylmethyl chloride by various aromatic and aliphatic hydrocarbon radicals in this way. On the other hand, Davis and Kipping (J., 1911, **99**, 300) were unable to prepare γγ-dibenzyl-*n*-hexane, $(C_6H_5\cdot CH_2)_2CEtPr$, by the action of magnesium propyl bromide on α-bromo-αα-dibenzylpropane, $(C_6H_5\cdot CH_2)_2CBrEt$; in every case, the product consisted mainly, if not entirely, of an unsaturated hydrocarbon. Späth (*Monatsh.*, 1913, **34**, 1965), who made an exhaustive study of the action of Grignard reagents on organic halogen derivatives, found that, although quaternary hydrocarbons were generally produced, the yield was always poor and a mixture of numerous products was obtained. It appeared, therefore, that the interaction of a Grignard reagent and a tertiary halide often takes quite an unexpected course and this conclusion is confirmed by the results described below.

A preliminary study of the proposed method was made with *β-bromo-α-phenyl-β-methylbutane*, a compound readily prepared from methyl ethyl ketone. This bromide reacted with magnesium ethyl bromide, with evolution of ethane and ethylene, but the product appeared to consist entirely of a mixture of the olefine, $C_6H_5\cdot CH{:}CMeEt$, and the saturated compound, $C_6H_5\cdot CH_2\cdot CHMeEt$, and the possible presence of a small proportion of the quaternary hydrocarbon could not be proved. Attempts to prepare a quaternary hydrocarbon by first converting the bromide into a Grignard reagent and then treating the product with ethyl bromide were also unsuccessful; although the bromide reacted with magnesium in the presence of dry ether, magnesium bromide separated even at 0° and a mixture of the saturated hydrocarbon and the olefine was formed. *β-Bromo-α-phenyl-β-benzylpropane*, which was easily obtained in a pure crystalline form, reacted with magnesium ethyl bromide with formation of a small proportion of *αδ-diphenyl-βγ-dibenzyl-βγ-dimethylbutane* (compare Späth, loc. cit.):

$$2CMeBr(CH_2Ph)_2 + 2MgEtBr = (CH_2Ph)_2CMe\cdot CMe(CH_2Ph)_2 + C_4H_{10} + MgBr_2.$$

The main product, however, as indicated by analysis, and by the evolution of ethane and ethylene, was a mixture of *αγ-diphenyl-β-methylpropane* (I) (Graebe, *Ber.*, 1874, **7**, 1627), and an olefine, $C_{10}H_{16}$, believed to be αγ-diphenyl-β-methyl-Δ^{α}-propene (II):

$$\text{(I).}\quad CHMe(CH_2Ph)_2 + C_2H_4 + MgBr_2 \xleftarrow{MgEtBr} CMeBr(CH_2Ph)_2 \xrightarrow{MgEtBr} C_2H_6 + MgBr_2 + CHPh{:}CMe\cdot CH_2Ph\ \text{(II.)}$$

The constitution of this olefine could not be established by

oxidising it to a mixture of benzoic acid or benzaldehyde and benzyl methyl ketone with potassium permanganate or ozonised oxygen, since only benzoic acid was obtained; this result was doubtless due to the fact that benzyl methyl ketone is itself very readily oxidised. The structure assigned to the olefine is rendered very probable by the known behaviour of other bromides similar to β-bromo-α-phenyl-β-benzylpropane (compare Orechov and Konovalov, *Ber.*, 1912, **45**, 861; Orechov and Meerson, *ibid.*, p. 1926).

β-Bromo-α-phenyl-β-benzylpropane reacted with magnesium benzyl chloride with the formation of a very small quantity of the quaternary hydrocarbon, *α-phenyl-ββ-dibenzylpropane*. The main product, however, was an olefine, doubtless identical with II:

$$CMeBr(CH_2Ph)_2 + CH_2Ph{\cdot}MgCl = (II.) + MgClBr + C_6H_5{\cdot}CH_3.$$

Unlike β-bromo-α-phenyl-β-methylbutane, β-bromo-α-phenyl-β-benzylpropane did not react with magnesium, even when iodine was added, so that the quaternary hydrocarbon could not be prepared by modifying the procedure. In boiling ethereal or benzene solution, the bromide reacted with sodium, but the above-described olefine was formed.

Tribenzylmethyl bromide (Schmerda, *Monatsh.*, 1909, **30**, 387), treated with magnesium ethyl bromide, gave a small yield of hexabenzylethane (Schmerda, *loc. cit.*), $2(CH_2Ph)_3CBr + 2MgEtBr = (CH_2Ph)_3C{\cdot}C(CH_2Ph)_3 + C_4H_{10} + 2MgBr_2$, but the main product was αγ-diphenyl-β-benzyl-Δ^{α}-propene (III): $(CH_2Ph)_3CBr + MgEtBr = (III.)\ CHPh{:}C(CH_2Ph)_2 + C_2H_6 + MgBr_2$. This olefine, which has been described by Orechov and Grinberg (*J. Russ. Chem. Phys. Soc.*, 1916, **48**, 1713) as a viscous liquid, was obtained in well-formed crystals, m. p. 42—43°. Tribenzylmethyl bromide was also treated with magnesium benzyl chloride; it gave a small amount of *tetrabenzylmethane*, but the product consisted mainly of III. The action of zinc ethyl on this bromide was also investigated, but the above olefine was the only product.

As there seemed to be indications that the halogen atom of tertiary halides is more readily displaced by a benzyl than by an ethyl group, the action was investigated of magnesium benzyl chloride on *β-bromo-α-phenyl-β-methylpropane*. A quaternary hydrocarbon of the desired type, *viz.*, α-phenyl-β-benzyl-β-methylpropane, was in fact produced, but about 50% of the product consisted of α-phenyl-β-methyl-Δ^{α}-propene (Klages, *Ber.*, 1904, **37**, 1721).

The results of these experiments show that in many cases the reaction between Grignard reagents and tertiary halogen derivatives does not follow the normal course. Späth (*loc. cit.*) expressed

the view that during this reaction the organic halide and the Grignard reagent undergo dissociation, so giving rise to free organic radicals:

$$R'X + RMgX = R' + R + MgX_2.$$

The existence of these radicals, however, is only momentary; those which are electropositive tend to unite together, but those which are more electronegative show a tendency to form olefines and paraffins containing the same number of carbon atoms as the radicals. The basis of Späth's classification into positive and negative radicals is not very obvious and his views do not seem to afford a very satisfactory explanation of the results summarised above.

A few attempts were made to obtain diketones of the type $C_6H_5 \cdot CO \cdot CR(CH_2 \cdot C_6H_5) \cdot CO \cdot CH_3$ in the hope that subsequent reduction might yield a quaternary hydrocarbon. *Benzylbenzoylacetone* was prepared, but on treatment with sodium ethoxide and ethyl bromide it gave ω-benzylacetophenone, an acetyl group being eliminated.

Experimental.

β-Bromo-α-phenyl-β-methylbutane, $C_6H_5 \cdot CH_2 \cdot CMeEtBr$, a colourless oil with a pleasant minty odour and an extremely irritating action on the eyes, was obtained in almost theoretical quantity by saturating benzylmethylethylcarbinol (Konovalov, *J. Russ. Chem. Phys. Soc.*, 1904, **36**, 228) with hydrogen bromide at the ordinary temperature. It decomposed when distilled even under 11 mm. and was therefore purified by washing it with dilute sodium carbonate solution and water (Found: Br = 34·0. $C_{10}H_{15}Br$ requires Br = 35·2%).

Action of Grignard Reagents on β-Bromo-α-phenyl-β-methylbutane.—When an excess of magnesium ethyl bromide was added to an ethereal solution of the bromide, a vigorous reaction immediately occurred, magnesium bromide was formed, and ethane and ethylene were evolved. The main product was an oil, practically the whole of which distilled between 195° and 205°. Its behaviour towards bromine and hydrogen bromide, and analyses of the bromo-derivatives thus obtained, indicated that it was a mixture of an olefine, believed to be α-phenyl-β-methyl-Δ^{α}-butene, and a saturated hydrocarbon, probably α-phenyl-β-methylbutane, b. p. 203—204° (Tafel and Hahl, *Ber.*, 1907, **40**, 3313). Since, from its boiling point, it could hardly contain an appreciable quantity of the expected quaternary hydrocarbon, and analysis showed the presence of a small proportion of benzylmethylethylcarbinol, the oil was not further examined.

A solution of the bromide in dry ether had no action on magnesium until a trace of iodine had been added; a vigorous reaction then set in and magnesium bromide separated even at 0°. The product was a mixture, b. p. 195—205°, apparently identical with that described above.

Dibenzylmethylcarbinol, $(C_6H_5 \cdot CH_2)_2CMe \cdot OH$, prepared from magnesium benzyl chloride and ethyl acetate, is a colourless, viscous, sweet-smelling liquid, b. p. 195—200°/14 mm. (with slight decomp.) (Found: C = 85·5; H = 8·0. $C_{16}H_{18}O$ requires C = 85·0; H = 8·0%).

β-*Bromo*-α-*phenyl*-β-*benzylpropane*, $(C_6H_5 \cdot CH_2)_2CMeBr$, obtained in good yield by saturating an ethereal solution of the unpurified carbinol with hydrogen bromide and recrystallising the product from light petroleum and from alcohol, formed well-defined, prismatic crystals, m. p. 78·5°. It loses hydrogen bromide when heated and cannot be distilled even under 0·2 mm. It is readily soluble in ether, alcohol, or benzene and sparingly so in light petroleum (Found: Br = 27·6. $C_{16}H_{17}Br$ requires Br = 27·7%).

Action of Magnesium Ethyl Bromide on β-*Bromo*-α-*phenyl*-β-*benzylpropane*.—A solution of the bromide in ether (1 vol.) was added slowly to magnesium ethyl bromide (4 vols.) at the ordinary temperature. The gas which was soon evolved, after being freed from ether with the aid of sulphuric acid, contained about 42% of ethane and 58% of ethylene. After 8 hours, the reaction mixture was boiled for 2 hours. The product, isolated in the usual way, was a slightly yellow oil. Its solution in alcohol (8 vols.) deposited crystals of αδ-*diphenyl*-βγ-*dibenzyl*-βγ-*dimethylbutane*,

$$(C_6H_5 \cdot CH_2)_2CMe \cdot CMe(CH_2 \cdot C_6H_5)_2,$$

which separated from much light petroleum in colourless plates, m. p. 171°; the yield was about 0·5 g. from 40 g. of the bromide (Found: C = 92·0; H = 8·3; *M*, cryoscopic in benzene, = 389. $C_{32}H_{34}$ requires C = 91·9; H = 8·1%; *M* = 418).

Separation of αγ-*Diphenyl*-β-*methylpropane* (I) and (?) αγ-*Diphenyl*-β-*methyl*-Δ^{α}-*propene* (II).—The main product, obtained as an oil when the above alcoholic mother-liquor was evaporated, distilled between 290° and 300°. It combined with bromine in chloroform solution, but the dibromide did not crystallise and very readily lost hydrogen bromide. Oxidation or treatment with sulphuric acid having failed to separate the olefine from the saturated hydrocarbon, the oil was saturated with hydrogen bromide, when about 50% of it was converted into crystalline β-bromo-α-phenyl-β-benzylpropane. The unchanged oil was separated from the bromide and treated with sodium amalgam and aqueous alcohol to reduce any remaining bromide. The final

product, b. p. 290—294°, was *αγ-diphenyl-β-methylpropane* (Found : C = 91·2; H = 8·4. $C_{16}H_{18}$ requires C = 91·4; H = 8·6%). Thus the quaternary hydrocarbon, α-phenyl-β-benzyl-β-methylbutane (calc., C = 90·8; H = 9·2%), was not among the products of the reaction.

The *olefine* (II), a colourless oil, b. p. 294—296°, was obtained by boiling the bromide with an excess of pyridine for 8 hours. It combined with bromine in chloroform solution, giving a dibromide which could not be crystallised and readily lost hydrogen bromide when it was heated (Found : C = 92·2; H = 7·6. $C_{16}H_{16}$ requires C = 92·3; H = 7·7%).

Action of Magnesium Benzyl Chloride on β-Bromo-α-phenyl-β-benzylpropane.—The Grignard reagent (4 mols.) did not react with the bromide in ether at the ordinary temperature. The ether was evaporated, and the residue heated at 100° for 2 hours. The product, isolated in the usual way, was an oil, a solution of which in alcohol deposited crystals of *α-phenyl-ββ-dibenzylpropane*, $(C_6H_5 \cdot CH_2)_3CMe$; these separated from alcohol in needle-shaped prisms, m. p. 113°, which were sparingly soluble in alcohol or light petroleum, but dissolved more readily in other organic solvents (yield about 5%) (Found : C = 91·5; H = 7·9; *M*, cryoscopic in benzene, = 294. $C_{32}H_{34}$ requires C = 92·0; H = 8·0%; *M* = 300). The main product, obtained as an oil when the alcoholic mother-liquor was evaporated, contained the olefine (II), but the probable presence of αγ-diphenyl-β-methylpropane (I) could not be proved owing to the impossibility of separating the dibenzyl which the oil contained.

Action of Magnesium Ethyl Bromide on Tribenzylmethyl Bromide.—Tribenzylmethyl bromide (Schmerda, *loc. cit.*), which is most conveniently prepared by saturating an ethereal solution of tribenzylcarbinol with hydrogen bromide, was treated in benzene solution with an excess of ethereal magnesium ethyl bromide; magnesium bromide separated at once and a gas, containing only a very small proportion of olefine, was evolved. After 2 hours, the reaction mixture was gently boiled for 1 hour. The product, isolated in the usual way, was a very viscous oil; from its solution in alcohol, colourless, cubical crystals gradually separated. This compound, after recrystallisation from alcohol, melted at 42—43° and was doubtless αγ-diphenyl-β-benzyl-Δ^{α}-propene (III) (compare Orechov and Grinberg, *loc. cit.*). Its identity was established by converting it into the crystalline dibromide, m. p. 127—128°, and also into tribenzylmethyl bromide with the aid of hydrogen bromide. When the alcoholic mother-liquor from the crystalline olefine was evaporated, there remained an oil from which hexa-

benzylethane was isolated by converting the olefine into tribenzylmethyl bromide (see above) and subsequently extracting the product with alcohol. From the alcoholic extract the hydrocarbon was deposited in crystals, m. p. 82—83°. Schmerda (*loc. cit.*) gives the m. p. 81—82° (Found: C = 92·4; H = 7·7. Calc. for $C_{44}H_{42}$, C = 92·6; H = 7·4%).

Tetrabenzylmethane, $C(CH_2{\cdot}C_6H_5)_4$.—Tribenzylmethyl bromide, dissolved in benzene, was added to an ethereal solution of excess of magnesium benzyl chloride, the solvents were then evaporated, and the residue was heated at 100° for 2 hours. The product, isolated in the usual way, was an oil, from which *tetrabenzylmethane* (yield 5%) was precipitated on the addition of alcohol. It separates from ether in cubic crystals, m. p. 164°, which are very sparingly soluble in alcohol or light petroleum, but dissolve more easily in other organic solvents (Found: C = 92·7; H = 7·5. $C_{29}H_{28}$ requires C = 92·5; H = 7·5%). The main product was αγ-diphenyl-β-benzyl-Δ^{α}-propene (III).

β-Bromo-α-phenyl-β-methylpropane, $C_6H_5{\cdot}CH_2{\cdot}CMe_2Br$, obtained by saturating dimethylbenzylcarbinol (Grignard, *Compt. rend.*, 1900, **130**, 1324) with hydrogen bromide and washing the product with sodium carbonate solution and water, is a colourless, pleasant-smelling liquid which loses hydrogen bromide very readily when it is warmed and does not distil unchanged under 11 mm. (Found: Br = 36·4. $C_{10}H_{13}Br$ requires Br = 37·5%).

α-Phenyl-β-benzyl-β-methylpropane, $(CH_2Ph)_2CMe_2$.—Reaction set in at once when the preceding bromide (1 mol.), dissolved in ether, was added to magnesium benzyl chloride (2 mols.); after 4 hours, the reaction mixture was boiled gently for 2 hours. The product, isolated in the usual way, consisted of an oil, which was separated by distillation into α-phenyl-β-methyl-Δ_{α}-propene, b. p. 181°, and a fraction of higher boiling point; the latter solidified when cold and crystallised from alcohol in prismatic needles, m. p. 68—69° (Found: C = 90·95; H = 9·0. $C_{17}H_{20}$ requires C = 91·1; H = 8·9%). *α-Phenyl-β-benzyl-β-methylpropane* boils at 293—294°, is readily soluble in most organic solvents, and has a somewhat sweet odour.

Benzylbenzoylacetone.—The sodium derivative of benzoylacetone, prepared from its constituents in ether, was isolated and boiled for 1 hour with an excess of benzyl chloride, the solution was filtered, and the unchanged benzyl chloride removed by distillation under reduced pressure. From an alcoholic solution of the residual dark brown oil, *benzylbenzoylacetone* was deposited in clusters of needle-shaped crystals, m. p. 60—61° (yield 50%). The compound is insoluble in aqueous potassium hydroxide and gives no coloration

with ferric chloride (Found: C = 80·6; H = 6·1. $C_{17}H_{16}O_2$ requires C = 80·95; H = 6·35%). When an alcoholic solution of benzylbenzoylacetone containing sodium ethoxide and ethyl bromide is kept at the ordinary temperature for 24 hours, sodium bromide separates, but the product is mainly ω-benzylacetophenone.

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UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 29th*, 1924.]

XVI.—*Transformation of Mandelonitrile to Mandelo-iso-nitrile.*

By CHARLES EDMUND WOOD and HAROLD SAMUEL LILLEY.

MANDELONITRILE which has been kept for some time becomes viscous and in some cases deposits a dark yellow solid, owing to transformation of the normal nitrile to the *iso*-form; such material gives a poor yield (50%) of mandelic acid on hydrolysis.

The rate of change of the nitrile to the *iso*-form is variable and depends on the purity of the potassium cyanide used in its preparation. Crude commercial potassium cyanide gives products which remain clear for a long period (4—5 days), but 95% potassium cyanide (Poulenc Frères) yields a nitrile in which the rate of change is much greater. The following results show the maximum observed rate of change with time in the nitrile and the corresponding reduction in the yield of mandelic acid :—

Time (days)	0	0·25	0·5	0·75	1·0	2·0	3·0	4·0
% Yield of acid	94·6	91·0	86·5	82·0	78·1	65·0	56·4	50·3

The yields of acid obtained do not correspond with the composition of the mixture hydrolysed, owing to a reversion of the *iso* to the normal form under the conditions of hydrolysis. The results indicate that, to give the best yield of acid, the nitrile should be rapidly separated and hydrolysed (compare Pape, *Chem. Ztg.*, 1896, 20, 90).

The change of the nitrile on standing is continuous, no reaction product other than the yellow solid appears to be formed, and a nearly theoretical yield of the *iso*nitrile is ultimately obtained. The reversibility of the reaction is indicated by the hydrolysis of the pure *iso*nitrile, which yields 38% of mandelic acid.

A similar case is that of the *cyclo*hexane analogue of mandelonitrile. The colourless, oily hexahydrobenzaldehydecyanohydrin

(Zelinsky and Gutt, *Ber.*, 1908, **41**, 2677) becomes dark and viscous on standing, and when hydrolysed gives as main product a dark brown tar and little hexahydromandelic acid. Investigation of the tar showed that the *iso*nitrile was present in the product hydrolysed.

EXPERIMENTAL.

Formation of Mandeloisonitrile (*α-Hydroxybenzylcarbylamine*) *from Mandelonitrile.*—Mandelonitrile on keeping deposits mandelo*iso*nitrile as a yellow solid which, after crystallisation from chloroform, melts at 196° (corr.) (Found: N = 10·7; M = 129 in chloroform, 136 in carbon tetrachloride, 130 in camphor. Calc., N = 10·6%; M = 133). The *iso*nitrile is fairly soluble in alcohol, ether, or benzene, more soluble in carbon tetrachloride, and insoluble in water. It darkens on standing in air, is not attacked by alkali, but is rapidly decomposed by dilute or concentrated mineral acids. With concentrated sulphuric acid, it gives a bright green colour, whereas the normal nitrile gives a red one (Schiff, *Ber.*, 1899, **32**, 2701).

The *iso*nitrile structure was confirmed by reduction of the compound to a secondary base, oxidation to a carbimide, and by examination of its hydrolytic products.

This compound is distinct from the yellow solid, m. p. 206°, obtained by Minovici (*Ber.*, 1899, **32**, 2206) by the action of hydrogen chloride on an ethereal solution of mandelonitrile, for which the formula $C_6H_5{\cdot}CH(CN){\cdot}C(OH)(CN){\cdot}C_6H_5$ was suggested. Even after repeated crystallisation, our compound melted at the temperature stated; moreover, it differs from Minovici's compound in its solubility in alcohol and ether and in its inability to form a salt, m. p. 222°, with hydrochloric acid.

Reduction.—The *iso*nitrile (5 g.) was heated with a solution of 25 g. of "hydros" * in 100 c.c. of a mixture of equal parts of alcohol and water for 30 minutes on the water-bath, the excess of hydros decomposed with warm hydrochloric acid, and the liquid filtered into concentrated aqueous ammonia, when *α-hydroxybenzylmethylamine*, $C_6H_5{\cdot}CH(OH){\cdot}NH{\cdot}CH_3$, was precipitated.

The crude product was purified by conversion to the ether-insoluble picrate, decomposition of the salt with ammonia, and crystallisation of the liberated base from petroleum (b. p. 60—80°). The low yield (50%) is probably due to sulphamation during reduction. The base is a yellowish-grey solid, m. p. 180° (decomp.), readily soluble in alcohol, ether, or mineral acids (Found: N = 10·3. $C_8H_{11}ON$ requires N = 10·2%). The *nitrosoamine*, prepared in the

* Stannous chloride or ammonium chloride and zinc dust may be employed.

usual way, is a yellow oil which solidifies on cooling. The *picrate*, prepared in ethereal solution, is a dark yellow, crystalline solid, m. p. 238° (decomp.) (Found: Picric acid = 62·1. $C_8H_{11}ON,C_6H_3O_7N_3$ requires 62·7%).

Oxidation.—An ethereal or carbon tetrachloride solution of the *iso*nitrile was heated with mercuric oxide (theor. quantity) on the water-bath for 1 hour. The dark red oil of disagreeable odour obtained on evaporating the filtered solution changed, on standing, to a black, amorphous mass, probably a polymeride. The oily carbimide could not be purified for analysis, but its structure was established by means of its reaction products.

The oil was treated with gaseous ammonia in carbon tetrachloride solution, when the red colour rapidly disappeared. The solution, on evaporation, deposited almost colourless crystals of the *carbamide*, $C_6H_5{\cdot}CH(OH){\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 76° (Found: N = 16·95. Theory requires N = 16·9%), readily soluble in water or alcohol, less soluble in benzene. The *nitrate* is fairly soluble in water, but mercuric chloride precipitates from neutral aqueous solutions the slightly yellow, almost insoluble *mercurichloride*,

$$C_6H_5{\cdot}CH(OH){\cdot}NH{\cdot}CO{\cdot}NH_2,HgCl_2$$

(Found: Hg = 45·58. Theory requires Hg = 45·83%).

The *picrate*, prepared in ethereal solution, was obtained as an orange, crystalline solid, easily soluble in ether or alcohol [Found: picric acid = 73·6. $C_6H_5{\cdot}CH(OH){\cdot}NH{\cdot}CO{\cdot}NH_2,2C_6H_3O_7N_3$ requires 73·3%].

Hydrolysis.—The *iso*nitrile rapidly dissolved when treated on the water-bath with concentrated hydrochloric acid (5 parts). The small quantity of tarry matter produced was removed, the filtrate distilled in steam, and benzaldehyde extracted from the distillate, which then showed, after neutralisation, the characteristic reducing properties of formic acid.

The benzaldehyde is produced by the decomposition of the primary base initially formed in the hydrolysis, which may be represented as follows:

$$OH{\cdot}CHPh{\cdot}NC \longrightarrow H{\cdot}CO_2H + OH{\cdot}CHPh{\cdot}NH_2 \longrightarrow Ph{\cdot}CHO + NH_3.$$

The amounts of formic acid and benzaldehyde found were not theoretical; in addition to the tarry matter deposited, a certain amount of mandelic acid was extracted.

By the hydrolysis of the pure *iso*nitrile for 3 hours under the above conditions, a 38% yield of mandelic acid was obtained. The mandelic acid was estimated by neutralisation of the filtered reaction product with ammonia, followed by addition of zinc sulphate or cadmium chloride solution; zinc or cadmium mandelate,

precipitated on standing and shaking, was filtered off, dried, and weighed. Small corrections (McKenzie, J., 1899, **75**, 969) were applied for the solubility of these salts. The use of the silver salt in the estimation is precluded owing to the presence of formic acid, and to a lesser extent, benzoic acid. Hence the reaction normal nitrile $\longrightarrow$ *iso*nitrile is reversible, proceeding under the conditions of hydrolysis from the *iso* to the normal form (compare Guillemard, *Compt. rend.*, 1907, **144**, 141). Further, when mixtures of the two forms are hydrolysed, the yield of mandelic acid is greater than that corresponding with the initial composition of the mixture. Also, on allowing the normal nitrile to stand, the yield of acid on hydrolysis cannot fall below 38%, although the change to the *iso*-form is complete.

The observed tarry matter consists probably of compounds produced by the action of ammonia on the nitrile (Schiff, *Ber.*, 1899, **32**, 2701).

Hydrolysis of Hexahydromandeloisonitrile.—The pure *iso*nitrile has not been isolated, but the normal form, kept for 2 months and then hydrolysed, gave large amounts of tarry matter and 20% of acid. The tarry product was polymerised hexahydrobenzaldehyde and its ammonia derivative, for by treatment with dilute caustic soda solution, followed by distillation in steam after acidification, the aldehyde was extracted from the distillate in quantity. Formic acid accompanied the viscous products.

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XVII.—*The Hydrolysis of Acylchloroamines in Water.*

By FREDERICK GEORGE SOPER.

THE slight extent of the reversible hydrolysis of chloroamines in water (Orton and Gray, *Brit. Assoc. Rep.*, 1913, 135), $:NCl + H_2O \rightleftharpoons :NH + HClO$, renders its quantitative study difficult, since it necessitates direct estimation of the concentrations of the hydrolysis products (as opposed to their estimation by difference), and, further, neither of the hydrolysis products is a sufficiently good electrolyte to allow of the application of sensitive electrical methods. Moreover, the one partition method available, that of estimation of the hypochlorous acid by distillation (Orton and Gray, *loc. cit.*), is, as will be shown later, complicated by the fact that the chloroamine is itself volatile.

In order to increase the hydrolysis of a chloroamine and thus

allow of the general application of methods available for the examination of homogeneous equilibrium, the concentration of one of the products of the hydrolysis may be still further reduced by its reversible combination with some other substance, the conditions of equilibrium with which are known. Substances considered for this purpose were hydrochloric acid, interacting with the hypochlorous acid to form chlorine, or an alkali, forming hypochlorite. Both these substances, however, may cause secondary reactions, the chlorine forming *C*-chlorinated products, whilst the alkali may cause hydrolysis of, and to a certain extent may form complexes with, the acylamine present. The use of another amine, which forms reversibly a chloroamine with the hypochlorous acid present, is free from the objections associated with the use of hydrochloric acid or an alkali, but it demands a knowledge of the hydrolysis equilibrium of *one* chloroamine before calculation of other hydrolysis constants becomes possible. *p*-Toluenesulphondichloroamide was selected as this standard chloroamine for reasons that have already been given (J., 1924, **125**, 1899).

When the hydrolysis of the chloroamine under investigation has been displaced, the method of examination employed is of a solubility type, and depends on the following considerations. *p*-Toluenesulphondichloroamide dissolves in solutions of anilides with the formation of the corresponding chloroamines:

$$C_7H_7\cdot SO_2\cdot NCl_2 + H_2O \rightleftarrows \begin{matrix} C_7H_7\cdot SO_2\cdot NHCl \\ \uparrow\downarrow \\ C_7H_7\cdot SO_2\cdot NH_2 \end{matrix} + HClO \overset{ArAcNH}{\rightleftarrows} ArAcNCl.$$

Hypochlorous acid is removed by combination with the added anilide and causes further solution and hydrolysis of the sulphondichloroamide. From the increase in the solubility of the sulphondichloroamide, as measured by the thiosulphate titre of the saturated solution, the concentrations of the chloroamines formed in solution can be calculated. This "solubility" of the sulphondichloroamide in a solution of an anilide is made up of the concentrations of the dichloroamide, the monochloroamide, the chloroamine formed from the anilide, and the hypochlorous acid. If a is the equilibrium concentration of the dichloroamide in millimols. in solution, T_1 the thiosulphate titre expressed as milliequivalents per litre, then

$$[C_7H_7\cdot SO_2\cdot NHCl] + [ArAcNCl] + [HClO] = (T_1 - 4a)/2,$$

or neglecting the [HClO], for reasons discussed below, and denoting the concentration of the chloroamine, ArAcNCl, formed from d millimols. of anilide by x and that of the sulphonmonochloroamide by b,

$$x + b = (T_1 - 4a)/2 = S \quad . \quad . \quad . \quad . \quad (1)$$

It is known that (J., 1924, **125**, 1906) at 25°,

$$[C_7H_7\cdot SO_2\cdot NHCl][HClO] = 8\cdot0 \times 10^{-4}\,[C_7H_7\cdot SO_2\cdot NCl_2] = 6\cdot27 \times 10^{-5} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and $$[C_7H_7\cdot SO_2\cdot NH_2][HClO] = 4\cdot9 \times 10^{-5}\,[C_7H_7\cdot SO_2\cdot NHCl] \quad (3)$$

while from the general conditions of equilibrium

$$[C_7H_7\cdot SO_2\cdot NH_2] = x - b \quad . \quad . \quad . \quad . \quad (4)$$

Combining (3) and (4),

$$[HClO](x - b)/b = 4\cdot9 \times 10^{-5};$$

eliminating HClO from (2),

$$(x - b)/b^2 = 0\cdot781;$$

and eliminating x from (1),

$$0\cdot781b^2 + 2b - S = 0 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This equation allows of the calculation in millimols., of b, of the concentration of hypochlorous acid, from (2), and of that of the chloroamine formed, from (1). The hydrolysis constant is given by the expression [HClO][anilide]/[chloroamine] = $[HClO]x/(d - x)$.

The omission of the hypochlorous acid concentration from equation (1) is permissible, because the progressive hydrolysis of the dichloroamide, caused by combination between the anilide and hypochlorous acid, results in an increase in the concentration of its hydrolysis product, $C_7H_7\cdot SO_2\cdot NHCl$, and hence in a diminution of the concentration of the hypochlorous acid, initially only 0·0079 millimols., since in presence of one solid phase, *viz.*, the sulphondichloroamide, the expression $[HClO][C_7H_7\cdot SO_2\cdot NHCl]$ is constant. It is this reduction in the concentration of the hypochlorous acid that makes the method of extensive use. For since the equilibrium concentration of the amine is measured by a difference, $d - x$, it is necessary that $x(= [ArAcNCl])$ should not approach d (the concentration of the anilide initially present) too closely in value, *i.e.*, the hydrolysis of the chloroamine should always be extensive. This is effected by the automatic diminution of the concentration of the hypochlorous acid, for the smaller the hydrolysis constant of the chloroamine (and therefore the greater the need for the displacement of its hydrolysis equilibrium), the smaller does the concentration of hypochlorous acid become, due to the accumulation of the sulphon*mono*chloroamide in the system.

The hydrolysis constants of the chloroamines of acetanilide, formanilide, aceto-*o*- and -*p*-toluidides, and *o*- and *p*-chloroacetanilides have been determined. The details of one determination and the mean values of K_h in the other cases are given in Table I.

TABLE I.

N-Chloroacetanilide.

Conc. of anilide. $\times 10^3$.	Thio. titre of sat. soln. $\times 10^3$.	b in $M \times 10^{-3}$.	x in $M \times 10^{-3}$.	HClO $M \times 10^{-7}$.	$K_h \times 10^7$.
0·5*M*	0·996*N*	0·161	0·182	3·89	6·80
1·0	1·322	0·232	0·274	2·70	7·15
2·0	1·784	0·317	0·420	1·88	7·44
5·0	2·734	0·506	0·706	1·24	7·53
				Mean	7·27

	$K_h \times 10^7$.		$K_h \times 10^7$.
N-Chloroformanilide	2·4	*No*-Dichloroacetanilide	6·9
N-Chloroaceto-*o*-toluidide ...	3·3	*Np*-Dichloroacetanilide	15·0
N-Chloroaceto-*p*-toluidide ...	22·0		

In Table II, the hydrolysis constants of the chloroamines examined are compared with the ionisation constants of similarly substituted compounds and with the equilibrium constants of the hydrolysis of anilides into amine and acid (MacBain and Davies, *Z. physikal. Chem.*, 1911, **78**, 369).

TABLE II.

Group.	K_h (chloro-amine).	K (anilide).	K_b (amine).	$1/K_a$ (phenol).	$1/K_a$ (benzoic acid).
H	$0·73 \times 10^{-6}$	4·1	$4·6 \times 10^{-10}$	$7·5 \times 10^5$	$16·7 \times 10^3$
o-CH_3	0·33	1·7	3·3	—	8·3
p-CH_3	2·2	6·4	20·0	—	19·4
o-Cl	0·69	0·14	—	1·3	0·76
p-Cl	1·5	2·2	1·3	2·5	10·7

The relative effects of the *o*-methyl and the *p*-methyl groups on the hydrolysis of the chloroamines and the ionisation of the amines are almost identical, as are also the relative effects of the *o*-chlorine and the *p*-chlorine atoms on the chloroamines and the phenols. The influence of the chlorine atom, compared with that of the hydrogen atom, on the hydrolysis of the chloroamines does not, however, appear to be similar to its influence on the ionisation of other substances.

The volatility of the chloroamine when its aqueous solutions are subjected to distillation at 25° causes the estimate of the percentage of free hypochlorous acid in an aqueous solution of *N*-chloroacetanilide (Orton and Gray, *loc. cit.*) to be high. Thus, on addition of successive quantities of acetanilide to the aqueous chloroamine solution, the ratio of the thiosulphate titre of the distillate to that of the original solution decreases to a minimum value of 0·20, independent of the concentration of the chloroamine solution. This behaviour is unlike that observed in the distillation of sodium hypochlorite in presence of excess of sodium hydroxide, the titre of the distillate then falling to zero. The thiosulphate titre of the distillate obtained from a 0·1% solution of *N*-chloroacetanilide was found (Orton and Gray, *loc. cit.*) to be 0·00268*N*, which, after

allowing for the volatility of the chloroamine, corresponds to a concentration of 0·00016 mol. of hypochlorous acid in the distillate or $5{\cdot}94 \times 10^{-5}$ mol. of hypochlorous acid in the chloroamine solution. The calculated hydrolysis constant of *N*-chloroacetanilide is then $6{\cdot}0 \times 10^{-7}$, a satisfactory confirmation of the value obtained by the solubility method ($7{\cdot}3 \times 10^{-7}$).

The limited solubility of anilides in water has prevented extensive examination in this medium. The primary object has been the determination of a few hydrolysis constants as a basis for testing theories of the mechanism of the chloroamine–chloroanilide transformation. The effect of substituents on the hydrolysis is being examined in other media.

EXPERIMENTAL.

Determination of the Solubility.—The determination of the solubility of *p*-toluenesulphondichloroamide in solutions of anilides was carried out in the same way as that in aqueous solutions of *p*-toluenesulphonamide (Soper, *loc. cit.*). The solution attained a practically constant titre after 3—6 hours. Since the chloroamines of anilides decompose slowly in water, owing to hydrolysis of the anilides to anilines (Orton and Gray, *loc. cit.*), one molecule of which removes a number of molecules of hypochlorous acid, the concentration of hypochlorous acid falls, and since the expression

$$[HClO][C_7H_7{\cdot}SO_2{\cdot}NHCl]$$

is constant in presence of the solid dichloroamide, the concentration of the monochloroamide increases. The net result is that the titre of the solution slowly increases on standing (*i.e.*, after 24 hours). The following figures, obtained during the solution of the dichloroamide in a solution of acetanilide ($2M \times 10^{-3}$), are typical.

Time	2	4	6	12	24 hours
Titre of 20 c.c. in *N*/500-thio.	13·71	17·80	17·86	17·92	18·05 c.c.

Distillation of Aqueous Chloroamine Solutions.—The diagram of the apparatus used has been given elsewhere (Soper, J., 1924, **125**, 2230). The thiosulphate titre of the solutions was taken before and after the distillation. There was no appreciable change during this process. No further decrease in the ratio of the titre of the distillate to that of the solution was obtained on increasing the acetanilide concentration from 0·02*M* to 0·05*M*.

In conclusion, I wish to express my thanks to Professor K. J. P. Orton, F.R.S., for his interest in this work.

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BANGOR. [*Received, September 27th*, 1924.]

XVIII.—*The Action of Amines on Semicarbazones. Part II.*

By FORSYTH JAMES WILSON and ARCHIBALD BARCLAY CRAWFORD.

IN continuation of previous work (J., 1922, **121**, 866) we have found that *l*-menthylamine reacts normally with acetonesemicarbazone to give active *acetone-δ-menthylsemicarbazone*, $CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + C_{10}H_{19}{\cdot}NH_2 = NH_3 + CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_{10}H_{19}$, from which *δ-menthylsemicarbazide*, $NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_{10}H_{19}$, and its *hydrochloride* have been obtained. These compounds, including the benzaldehyde derivative, are lævorotatory in alcoholic solution.

The action of esters of amino-acids on semicarbazones was next investigated. Ethyl *m*-aminobenzoate and acetonesemicarbazone reacted normally on heating, $CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_2{\cdot}C_6H_4{\cdot}CO_2Et = CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Et + NH_3$, giving *acetone-δ-3-carbethoxyphenylsemicarbazone* in good yield, from which *δ-3-carbethoxyphenylsemicarbazide*, $NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Et$, and its *hydrochloride* were obtained. Ethyl *p*-aminobenzoate also reacted normally with benzophenone- and acetone-semicarbazone (in the latter case with poor yield), giving the ketonic *δ-4-carbethoxyphenylsemicarbazones*, $CR_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Et$, both of which underwent complete decomposition when hydrolysis was attempted.

Methyl *o*-aminobenzoate reacted somewhat differently. In view of what follows, care was taken in all these cases to use dry materials and dry solvents so as to avoid any risk of hydrolysis. The ester, on heating with benzophenonesemicarbazone (molecular quantities), gave *3-diphenylmethyleneaminotetrahydroquinazoline-2 : 4-dione* (I),

$$C_6H_4{<}\begin{matrix}NH_2\\CO_2Me\end{matrix} + NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CPh_2 = NH_3 + MeOH + C_6H_4{<}\begin{matrix}NH{\cdot}CO\\CO{-}N{\cdot}N{:}CPh_2\end{matrix}\quad(I.),$$

this, on hydrolysis with acid, giving benzophenone and 3-aminotetrahydroquinazoline-2 : 4-dione (II), $C_6H_4{<}\begin{matrix}NH{\cdot}CO\\CO{-}N{\cdot}NH_2\end{matrix}$, described by Kunckell (*Ber.*, 1910, **43**, 1021). In addition, methyl alcohol, benzophenonecarbohydrazone (III), tetrahydroquinazoline-2 : 4-dione (IV), and small quantities of diphenyl ketazine and hydrazodicarbonamide were produced.

Borsche and Merkwitz have shown (*Ber.*, 1904, **37**, 3177) that benzophenonesemicarbazone, on heating, gives (III), presumably by interaction with the hydrazone, $CPh_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_2{\cdot}N{:}CPh_2 = NH_3 + CO(NH{\cdot}N{:}CPh_2)_2$ (III), the hydrazone appar-

ently resulting from the semicarbazone by loss of cyanic acid, $CPh_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 = CPh_2{\cdot}N{\cdot}NH_2 + HNCO$. In the present instance, the formation of (III) and (IV), the latter investigated, among others, by Griess (*Ber.*, 1869, **2**, 416), can be explained as resulting from the ester and the semicarbazone,

$$C_6H_4\!<\!\begin{matrix}NH_2\\CO_2Me\end{matrix} + \begin{matrix}NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CPh_2\\NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CPh_2\end{matrix} = NH_3 + MeOH + C_6H_4\!<\!\begin{matrix}NH{\cdot}CO{\cdot}NH{\cdot}N{:}CPh_2\\CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}N{:}CPh_2,\end{matrix}$$

which then gives (III) and (IV), the diphenyl ketazine and the hydrazodicarbonamide being produced by the decomposition of the semicarbazone as shown by Borsche and Merkwitz,

$$2CPh_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 = CPh_2{:}N{\cdot}N{:}CPh_2 + NH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2.$$

The interaction of acetonesemicarbazone with methyl *o*-aminobenzoate proceeded quite abnormally: as before, molecular quantities were employed and care was taken to use dry solvents. The acetone derivative (V) expected from the scheme $CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + C_6H_4\!<\!\begin{matrix}NH_2\\CO_2Me\end{matrix} = NH_3 + MeOH + C_6H_4\!<\!\begin{matrix}NH{\cdot}C\,O\\CO{-}N{\cdot}N{:}CMe_2\end{matrix}$ (V), was not produced; the products were ammonia, methyl alcohol, 3-aminotetrahydroquinazoline-2 : 4-dione (II) (the chief solid product, amounting to about half of the semicarbazone used), a considerable amount of dimethyl ketazine, small quantities of tetrahydroquinazoline-2 : 4-dione (IV) and of a *substance*, m. p. 420°, which could not be identified; it is noteworthy that no hydrazodicarbonamide was formed.

A different explanation is necessary in this case. It may be assumed that (V) 3-iso*propylideneaminotetrahydroquinazoline*-2 : 4-*dione* (prepared by another method and described below) is first produced with formation of ammonia and methyl alcohol and that it may react further in one of two ways. It may decompose as follows,

$$2C_6H_4\!<\!\begin{matrix}NH{\cdot}C\,O\\CO{-}N{\cdot}N{:}CMe_2\end{matrix} = CMe_2{:}N{\cdot}N{:}CMe_2 + C_6H_4\!<\!\begin{matrix}NH{\cdot}C\,O\\CO{-}N\end{matrix}\!>\!\begin{matrix}C\,O{\cdot}NH\\N{-}{-}CO\end{matrix}\!>\!C_6H_4 \quad \text{(VI.)}$$

A substance of the composition represented by (VI) was not obtained (the unidentified substance of m. p. 420° giving quite different analytical results); moreover it was found, as mentioned later, that (V) did not behave in this way on heating. The other possibility, and the one which we regard as the probable explanation, is that (V) reacts with acetonesemicarbazone to give dimethyl ketazine and the intermediate carbamino-derivative (VII),

$$C_6H_4\langle\begin{matrix}NH\cdot CO\\ CO-N\cdot N{:}CMe_2\end{matrix} + NH_2\cdot CO\cdot NH\cdot N{:}CMe_2 = CMe_2{:}N\cdot N{:}CMe_2 + C_6H_4\langle\begin{matrix}NH\cdot CO\\ CO-N\cdot NH\cdot CO\cdot NH_2\end{matrix} \quad \text{(VII.)}$$

which then by loss of cyanic acid gives (II).

Borsche and Merkwitz (*loc. cit.*) apparently assume loss of cyanic acid in a similar case. Auwers and others (*Annalen*, 1924, **435**, 277) have shown that tetrahydroindazole-2-carbonamide loses cyanic acid (identified as cyanuric acid) on heating at 160°, $C_6H_4\langle\begin{matrix}CH\\ N\end{matrix}\rangle N\cdot CO\cdot NH_2 \rightarrow C_6H_4\langle\begin{matrix}CH\\ N\end{matrix}\rangle NH$. Similarly, Posner (*Ber.*, 1901, **34**, 3976) found that compounds of the type $NH_2\cdot CO\cdot\overset{R}{N}\!\!=\!\!\overset{RC{:}CH\cdot CR}{N}$ (R = alkyl), obtained from semicarbazide and diketones, give with silver nitrate the derivative $Ag\overset{R}{N}\!\!=\!\!\overset{RC{:}CH\cdot CR}{N}$: when R = Ph, the carbamino-compound is not formed on heating the reactants, the product being 3 : 5-diphenylpyrazole. The substance (IV) probably results, together with (II), by interaction of (VII) with the ester:

$$C_6H_4\langle\begin{matrix}NH\cdot CO\\ CO-N\end{matrix}\begin{matrix}NH_2\\ CO\\ NH\end{matrix} + \begin{matrix}MeCO_2\\ NH_2\end{matrix}\rangle C_6H_4 =$$

$$\text{(IV.) } C_6H_4\langle\begin{matrix}NH\cdot CO\\ CO-NH\end{matrix} + \text{(II.) } C_6H_4\langle\begin{matrix}NH\cdot CO\\ CO-N\cdot NH_2\end{matrix} + MeOH.$$

To test these explanations, (V) was prepared by boiling ordinary undried acetone with (II); curiously enough, dried acetone did not react even on prolonged boiling, ββ-dichloropropane also proved unreactive. This substance (V) was easily hydrolysed into the parent compounds by water and by hot solvents containing water. It was scarcely affected by heating even at 220° for 2½ hours, it charred slightly and there was a slight odour of dimethyl ketazine, but most of the substance was recovered unchanged. Molecular quantities of (V) and acetonesemicarbazone, on heating, gave dimethyl ketazine and (II), this being in accordance with the explanation advanced by us.

This work will be continued.

Experimental.

l-Menthylamine and Acetonesemicarbazone.—The *l*-menthylamine, prepared by the method of Beckmann (*Annalen*, 1889, **250**, 325) and of Wallach (*ibid.*, 1893, **276**, 327), was distilled directly in a current of hydrogen into a polarimeter tube; it gave $[\alpha]_D^{20}$ — 39·41°

[Wallach records $-38{\cdot}07°$; Tutin and Kipping (J., 1904, **85**, 69) record $-39{\cdot}92°$].

Equimolecular quantities, previously heated to 165°, were mixed and kept at this temperature for 15 minutes, when solution with copious evolution of ammonia took place. The cooled melt, dissolved in a little alcohol, was poured into dilute acetic acid, the solid which separated dissolved completely in hot alcohol, from which, on cooling, active *acetone-δ-menthylsemicarbazone* was deposited in clusters of small, colourless needles, m. p. 128° (Found : N = 16·62, 16·73. $C_{14}H_{27}ON_3$ requires N = 16·60 %). 0·5024 Gram in 25 c.c. of absolute alcohol gave $\alpha_D^{20°} - 2{\cdot}612°$ ($l = 2$), whence $[\alpha]_D^{20°} - 64{\cdot}93°$. Yield 65 %. The substance was soluble in the usual organic solvents.

Active δ-Menthylsemicarbazide.—The semicarbazone was heated at 70° with *N*-hydrochloric acid (5 parts) until completely dissolved; the residue obtained by evaporation under reduced pressure was recrystallised from alcohol, which gave *δ-menthylsemicarbazide hydrochloride* as a gelatinous mass; after suction and washing with ether, it assumed a fibrous, apparently non-crystalline appearance and melted at 203—204° (Found : Cl=14·02, 14·22. $C_{11}H_{23}ON_3$,HCl requires Cl = 14·22%). 0·5024 Gram in 25 c.c. of absolute alcohol gave $\alpha_D^{20°} - 2{\cdot}62°$ ($l = 2$), whence $[\alpha]_D^{20°} - 65{\cdot}18°$. It was soluble in alcohol or hot water, insoluble in ether or benzene, and could not be obtained in a definitely crystalline form. *δ-Menthylsemicarbazide*, obtained by dissolving the hydrochloride in hot dilute alcohol, adding sodium hydroxide solution in slight excess, and then immediately diluting and cooling in ice, crystallised from light petroleum containing a little benzene in microscopic prisms, m. p. 138° (Found : N = 19·89, 19·83. $C_{11}H_{23}ON_3$ requires N = 19·71%). 0·4994 Gram in 25 c.c. of absolute alcohol gave $\alpha_D^{20°} -3{\cdot}11°$ ($l = 2$), whence $[\alpha]_D^{20°} - 77{\cdot}94°$. It was soluble in the usual organic solvents on heating : solutions cannot be kept, as they become green after one day. Addition of ethereal hydrogen chloride in slight excess to an absolute alcoholic solution precipitated the gelatinous hydrochloride. The *benzylidene* derivative, obtained by shaking an alcoholic solution of the hydrochloride with a little benzaldehyde and then adding a little water, solidified on standing and crystallised from alcohol, in which it was very soluble, in fine, rhombic prisms, m. p. 111° (Found : N = 13·96. $C_{18}H_{27}ON_3$ requires N = 13·95%). 1·898 Grams in 100 c.c. of absolute alcohol gave $\alpha_D^{20°} - 1{\cdot}79°$ ($l = 2$), whence $[\alpha]_D^{20°} - 47{\cdot}18°$. Solutions became green on standing.

Ethyl m-*Aminobenzoate and Acetonesemicarbazone.*—The two substances (1·6 mols. of the latter) were heated at 165° until the

evolution of ammonia began to slacken (20 minutes). The cooled melt was gently heated with a little alcohol, which, after filtration from hydrazodicarbonamide, deposited a solid on cooling; this was washed with a little alcohol and recrystallised from this solvent. A little more hydrazodicarbonamide was deposited followed by colourless plates of *acetone*-δ-3-*carbethoxyphenylsemicarbazone*, m. p. 146° (Found: N = 15·94, 16·02. $C_{13}H_{17}O_3N_3$ requires N = 15·97%). It was moderately soluble in alcohol, very soluble in pyridine, sparingly soluble or insoluble in other solvents. Yield 80%. Hydrolysis was effected by covering the substance with 2½*N*-hydrochloric acid and warming to 70°; the solid which separated on cooling in ice gave, after recrystallisation from alcohol, prisms of δ-3-*carbethoxyphenylsemicarbazide hydrochloride*, m. p. 172° (Found: Cl = 13·56, 13·72. $C_{10}H_{13}O_3N_3$,HCl requires Cl = 13·68%); it was readily soluble in hot (not very soluble in cold) water and hot alcohol, and reduced Fehling's solution and ammoniacal silver nitrate. δ-3-*Carbethoxyphenylsemicarbazide*, prepared in the usual manner from this salt with sodium hydroxide, separated from benzene in small prisms, m. p. 119°; it was very soluble in alcohol, chloroform, or hot benzene, and sparingly soluble in water (Found: N = 18·87, 18·88. $C_{10}H_{13}O_3N_3$ requires N = 18·83%). The *benzylidene* derivative, prepared from a hot aqueous solution of the hydrochloride and benzaldehyde, separated from alcohol in fine, hair-like needles, m. p. 144°, very soluble in most solvents except water (Found: N = 13·62, 13·50. $C_{17}H_{17}O_3N_3$ requires N = 13·50%).

Ethyl p-*Aminobenzoate and Benzophenonesemicarbazone.*—The semicarbazone was added during 1 hour to the ester (2 mols.) heated at 230°; a gentle evolution of ammonia took place and the heating was continued for 15 minutes after the last addition. The alcoholic extract of the cooled melt, after filtering from hydrazodicarbonamide, was poured into dilute acetic acid to remove excess of ester. The solid which separated on standing was extracted with cold toluene; the insoluble portion on recrystallisation from benzene gave pearly plates of *benzophenone*-δ-4-*carbethoxyphenylsemicarbazone*, m. p. 168° (Found: N = 11·03, 10·68. $C_{23}H_{21}O_3N_3$ requires N = 10·85%). The toluene extract contained diphenyl ketazine and benzophenonecarbohydrazone. The substance was soluble in most organic solvents, but almost insoluble in cold benzene, toluene, or light petroleum; exposure to light converted it without change of melting point into a lemon-yellow modification which gave colourless solutions. Yield about 57%.

Ethyl p-*Aminobenzoate and Acetonesemicarbazone.*—The semicarbazone was added during 20 minutes to the ester (1 mol. of

each) heated at 190—200°. The alcoholic extract of the cooled melt, filtered from a small amount of hydrazodicarbonamide, was evaporated, and the residue recrystallised from alcohol. The crystals obtained were washed with cold acetone to dissolve a small quantity of a *substance* which was not identified (prisms from acetone, m. p. 130°; found, N = 14·2%); several recrystallisations from alcohol gave hexagonal tablets of *acetone-δ-4-carbethoxyphenylsemicarbazone*, m. p. 194°. There was some difficulty in separating it from a very small amount of a powdery *substance*, m. p. 210°, which had almost the same solubility. The estimation of nitrogen in the semicarbazone offered considerable difficulty, the results being high and not concordant, due possibly to the production of methane (compare Haas, J., 1906, **59**, 570; Dunstan and Carr, P., 1896, **12**, 48): a 2-metre tube charged with lead chromate gave satisfactory results (Found: N = 16·18, 16·22. $C_{13}H_{17}O_3N_3$ requires N = 15·97%). The substance was soluble in alcohol or hot benzene, slightly soluble in hot acetone, insoluble in other solvents. Yield about 13%.

Methyl o-*Aminobenzoate and Benzophenonesemicarbazone.*—Molecular quantities were heated at 210° for 40 minutes; ammonia was evolved and methyl alcohol distilled over. The melt on extraction with boiling benzene gave a residue which was shown by treatment with hot pyridine to consist of a little hydrazodicarbonamide and tetrahydroquinazoline-2 : 3-dione. Concentration of the benzene extract gave a mixture, from which *3-diphenylmethyleneaminotetrahydroquinazoline-2 : 4-dione* was isolated by fractionally precipitating a chloroform solution with light petroleum. Concentration of these mother-liquors gave benzophenonecarbohydrazone. Further concentration of the benzene extract yielded a little diphenyl ketazine.

3-Diphenylmethyleneaminotetrahydroquinazoline-2 : 4-dione crystallised from alcohol in large prisms, m. p. 240°, and was moderately soluble in hot chloroform or hot pyridine, insoluble in ether (Found: N = 12·32, 12·54. $C_{21}H_{15}O_2N_3$ requires N = 12·31%). Boiling for ½ hour with 2½*N*-hydrochloric acid effected hydrolysis into benzophenone and 3-aminotetrahydroquinazoline-2 : 4-dione. Kunckell obtained the hydrochloride from the base and alcoholic hydrogen chloride; evidently aqueous acid did not produce this salt.

If the reaction product is worked up in the usual way with acetic acid, the 3-amino-compound is obtained and not the benzophenone derivative.

Methyl o-*Aminobenzoate and Acetonesemicarbazone.*—Equimolecular quantities, heated at 195° for 30—40 minutes, gave ammonia and a distillate containing methyl alcohol and dimethyl ketazine;

water, acetone, or hydrazine was not present. A white sublimate, very small in amount and probably ammonium carbamate, gradually formed and the melt ultimately solidified; it was then extracted with a little boiling benzene to remove resinous matter and unchanged ester. The residue was washed with light petroleum and fractionally recrystallised from pyridine, which dissolved it completely, indicating absence of hydrazodicarbonamide. The first crop of crystals consisted of 3-aminotetrahydroquinazoline-2 : 4-dione, concentration yielded large, regular, efflorescent prisms, almost complete evaporation gave tetrahydroquinazoline-2 : 4-dione. The prisms, after recrystallisation from pyridine, charred at 390° on slow heating but melted at 420° in a previously heated bath (sodium-potassium nitrates). This substance, which could not be identified, contained about 32% of pyridine of crystallisation which was expelled at 105°; analysis then gave: C = 60·32; H = 4·00; N = 17·41; O (by diff.) = 18·27. The amount of this compound was relatively small; it was insoluble in the usual solvents, including hydrochloric acid, soluble in pyridine or sodium hydroxide. The solution in concentrated sulphuric acid became pink on standing.

3-iso*Propylideneaminotetrahydroquinazoline*-2 : 4-*dione*, obtained by boiling the 3-amino-compound with ordinary undried acetone until completely dissolved (5 hours), crystallised from dry acetone in prisms, m. p. 212° (Found: N = 19·55, 19·58. $C_{11}H_{11}O_2N_3$ requires N = 19·35%). It was soluble in the usual organic solvents except ether and light petroleum; crystals from benzene were efflorescent, containing apparently solvent of crystallisation. A mixture of this substance with acetonesemicarbazone, on heating at 190° for 35 minutes, melted at first and then gradually solidified, ammonia was evolved, and dimethyl ketazine distilled in quantity. The solid, after removal of tarry matter by washing with ether and benzene, was identified as 3-aminotetrahydroquinazoline-2 : 4-dione: the evolution of ammonia was probably due to a decomposition of the semicarbazone, which gives this gas on heating.

The various substances mentioned were fully characterised as such by their properties and, if necessary, by analysis and preparation of derivatives.

In conclusion, we wish to thank the Carnegie Trust for the Universities of Scotland for a grant which has partly defrayed the expenses of this work.

THE ROYAL TECHNICAL COLLEGE,
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XIX.—*Banded Bituminous Coal. Studies in the Composition of Coal.*

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER.

As the result of an investigation into the chemical nature of the ingredients of banded bituminous coal (J., 1919, **115**, 619), it was found that the chief differences between them were expressed by a regular gradation in composition and in properties which could be accounted for by assuming the occurrence in each, in different proportions, of "reactive" and "inert" types of compounds. We are now able to offer as the result of later work, more particularly that on dopplerite (J., 1922, **121**, 2345), an explanation as to the character of these presumed "reactive" and "inert" constituents.

The various plant entities and residues that have contributed to the formation of the organic substance of coal can conveniently be grouped according as they are:

(1) *Resistant to decay.* Amongst the more important members of this group are: (*a*) Spore-exines and cuticular tissues; and (*b*) resins.

(2) *Subject to decay.* The members of this group are either: (*a*) Organised, such as cellulosic and lignified tissues; or (*b*) amorphous, the contents of plant cells.

(3) *The products of decay.* The ulmins.

An accumulation of plant remains immediately after deposition consists mainly of the first two groups, but in an older deposit, such as a peat bed, certain changes have taken place. The members of group 1 are still present in an apparently unaltered form. The cellulose and lignin of group 2, however, have suffered decay, undergoing such minor alterations as dehydration produces, or becoming ulmified (probably in conjunction with certain of the cell-contents), or disappearing altogether. According to Fischer and Schrader (*Brennstoff Chem.*, 1921, **2**, 23), the lignin alone survives in any form, the cellulose of necessity vanishing (being converted into liquid and gaseous products through the agency of bacteria), but we cannot regard this view as either proved or probable, and consider that ulmins can be produced from any plant material of carbohydrate type. Judging from the nature of peat, ulmification is the main chemical process during the decay of plants and it proceeds further the older the deposit: thus, whilst a young peat may yield only 10 or 20% of material soluble in alkalis, from an older peat as much as 70 or 80% can be extracted.

In a deposit of the age of coal, it cannot be expected that the

materials of any of the three groups will remain unaltered. Spore-exines and cuticular tissues may not be much changed, nor need the resins, but the cellulose that is not totally destroyed will in large part be converted, together with the more resistant lignin and part of the cell-contents, into the amorphous ulmins of group 3 (or products derived from them). There will also be material corresponding with group 2 (*a*), consisting of altered (but apparently not ulmified) woody tissues, such as compose many lignites and are recognisable in many bituminous coals. We have at present no knowledge as to what becomes of the non-ulmified portions of the cell-contents. As they finally appear in the coal, cell-wall structures, group 2 (*a*), may not differ much chemically from the amorphous ulmins, but the materials of group 1 differ markedly.

The more recent beds of plant remains, the peats, contain a large amount of alkali-soluble material, the amount increasing with the age of the deposit: but "older" fuels, such as brown coals and lignites, contain comparatively little, whilst bituminous coals, unless they have been considerably weathered, usually contain none. This diminishing content of alkali-soluble material, after a certain stage has been passed, would seem to be due to a change in the character of the ulmins, through condensation, dehydration and loss of carboxyl (with the formation of anhydrides and lactones) whereby their usual property of dissolving in alkalis to form dark brown solutions is lost. The alkali-soluble ulmins that surround and permeate the plant structures in an old peat (see J., 1922, **121**, 2345) may be presumed to have their counterpart in bituminous coal in the amorphous cementing material (insoluble in alkalis) in which the numerous plant structures are embedded.

We have already (*loc. cit.*, p. 2354) instituted a comparison and shown the similarity between dopplerite, a typical peat ulmin which occurs segregated in bands in some peat bogs, and vitrain, the brilliant structureless ingredient of banded bituminous coal. By analogy, there should also be a close relationship between all the amorphous cementing material of bituminous coal, whether segregated, as in a vitrain, or diffused, as in a clarain and a durain, and the amorphous ulmins that form so large a part of the older peats, and this relationship should extend to the amounts of amorphous material normally contained in the two fuels.

The correctness of this suggestion can be deduced from the data obtained during the study of the chemical nature of the ingredients of banded bituminous coal, referred to at the beginning of this paper.

The "reactivity" of the vitrain, clarain, and durain of Hamstead coal, as measured by their susceptibility to attack by solvents

and reagents and by the amounts of liquid and gaseous products yielded on destructive distillation, was found to diminish in the ratio 1·0 : 0·9 : 0·7, taking the ingredients in the order named, and it was concluded that the amounts of "reactive" material they contained diminished in the same proportion. Of the absolute amounts of "reactive" and "inert" materials present in any one of the ingredients, no conclusion could be drawn at the time the experiments were made, but with the recognition of vitrain as related to the nearly homogeneous ulmin, dopplerite, it follows that the bulk of vitrain should be regarded as "reactive."

Whence, since its composition had been found to be similar in all three ingredients, it must be concluded that the reactive material of a clarain and a durain is essentially an insoluble derivative of the ulmins and that in the clarain and durain of Hamstead coal it is present to the extent of about 90 and 70%, respectively. Actually, the vitrain contained a certain amount of material other than insoluble ulmins (resins, for example), so that these figures should be reduced somewhat.

It is difficult to judge from an examination of transparent sections of coal as to the proportions of amorphous and organised material present, but even if, as appeared, there is in the Hamstead durain, for example, a greater proportion of plant tissues than the 30% indicated by calculation, there are grounds for the belief that some plant remains in coal (woody tissues in particular), although they retain their organised structures, have been partially ulmified and thus function as "reactive" material. Otherwise, the plant entities (especially those of group 1) must constitute what we have termed the "inert" material of coal.

DEPARTMENT OF FUEL TECHNOLOGY,
SHEFFIELD UNIVERSITY. [*Received, October 17th*, 1924.]

XX.—*The Oxidation of Banded Bituminous Coal at Low Temperatures. Studies in the Composition of Coal.*

By WILFRID FRANCIS and RICHARD VERNON WHEELER.

Of the methods that have been used for studying the chemical composition of coal, attack by reagents has not, in general, yielded much information. The majority of the reagents used have been oxidants, such as nitric acid or Schultze's solution, and these either yield intractable gelatinous substances—the ulmins and their substitution products—or, ultimately, fatty acids, usually oxalic

acid. The use of a milder oxidant, such as atmospheric air at low temperatures, enables progressive changes in the character of the coal-substance to be studied, and, apart from the importance that a study of the oxidation of coal by air has in relation to its spontaneous combustion, many of the observations made throw light on the character of some of the ingredients of coal and thus help towards an understanding of its constitution.

The atmospheric oxidation or "weathering" of coal has been found to increase the proportion of substances extractable by alkaline solutions—the ulmin compounds—or even to produce such substances where apparently none existed previously. For example, Dennstedt and Bunz (*Z. angew. Chem.*, 1908, **25**, 1825), by heating a number of finely-powdered coals in open vessels during several days at 130—150°, showed that the effect of oxidation was, in some instances, to produce as much as 30 to 36% of ulmin compounds. Mahler (*Ann. Mines*, 1913, **4**, 163) passed a slow stream of air during long periods through coal heated at low temperatures and found that traces of formic acid, methyl alcohol and acetone, and larger quantities of acetic acid, were present in the condensed products of oxidation, whilst the coals themselves became increasingly soluble in aqueous potassium hydroxide and their temperatures of initial decomposition decreased as oxidation proceeded. If the temperature at which oxidation was effected was higher than 250°, the ulmin compounds (soluble in potassium hydroxide) formed at lower temperatures began to decompose.

The present research has as its object the tracing of the changes that take place in the character and composition of the coal conglomerate as oxidation slowly proceeds; and, more particularly, the comparison of the behaviour of the macroscopically distinct ingredients, into which most bituminous coals can readily be separated, when subjected to similar treatment. For, inasmuch as these banded ingredients, which Stopes has provisionally named vitrain, clarain, durain and fusain (*Proc. Roy. Soc.*, 1919, *B*, **90**, 470), have been shown to possess markedly different chemical characteristics even when taken from contiguous portions of the same lump of coal (see Tideswell and Wheeler, J., 1919, **115**, 619; Baranov and Francis, *Fuel*, 1922, **1**, 219), an intimate study of the chemistry of "coal" must of necessity treat of each ingredient separately; whilst a comparison of the differences that exist between the ingredients which together form the coal as it occurs in nature throws light on the manner of its formation.

The coal chosen for this work was from the Top Hard seam at the East Kirkby Colliery, Nottinghamshire, a detailed examination of which has been recorded by Baranov and Francis (*loc. cit.*).

The vitrain, clarain, and durain bands in this coal are sharply differentiated, and it contains a fair proportion of fusain. No experiments were made with the clarain portion, since previous work led us to believe that the results would be intermediate between those for the vitrain and durain portions. The method of experiment was, briefly, to draw a slow current of moist air through weighed samples (50 g.) of the three ingredients in the form of powder (through a 60's and on a 90's sieve) contained in glass tubes which could be maintained at a constant temperature during prolonged periods. After passing through the coal, the air bubbled into a measured volume of cold distilled water to condense any liquid or soluble gaseous products. At stated intervals this water was examined and changed and a small fraction (5 g.) of each coal was removed from the tubes for analysis.

Oxidation at 100°.

Liquid and Gaseous Products.—The treatment of the coals with air at 100° was carried out in four stages, the first of two months' and the remainder each of 1 month's duration. The distilled water through which the air bubbled after leaving the coals had, in each instance, acquired a milky appearance * by the end of the first period and had increased in volume. Tests were made for alkalinity or acidity, formaldehyde, acetone, acetaldehyde, and methyl and ethyl alcohols. The chief results, expressed approximately as percentages on the coals, are recorded in Table I.

TABLE I.

		Period I (two months).	Period II (one month).	Period III (one month).	Period IV (one month).
Vitrain	Formaldehyde	0·007	0·017	0·007	nil
	Methyl alcohol	0·014	0·006	nil	,,
	Acids	0·040	0·006	trace	,,
Durain	Formaldehyde	0·002	0·010	nil	,,
	Methyl alcohol	0·014	0·002	,,	,,
	Acids	0·004	trace	trace	,,
Fusain	Formaldehyde	nil	0·010	nil	,,
	Methyl alcohol	,,	0·004	,,	,,
	Acids	,,	trace	trace	,,

None of the solutions contained acetone or acetaldehyde, nor could any trace of ethyl alcohol be detected. The acids appeared to be either formic or acetic acid; sulphurous acid, which might have been derived from pyrites or sulphur compounds in the coals, was absent, nor was the acidity due to carbon dioxide in solution. The production of formaldehyde and methyl alcohol was not

* This was found to be due to bacterial growths, presumably derived from the coals; it disappeared during subsequent periods of the oxidation.

continuous, the liquids in the wash-bottles after the fourth oxidation period remaining apparently pure water; we believe that they were produced from methane occluded in the coals, probably by the action of ozone formed as the air bubbled through the wash-bottles leading to the coal samples.

Changes in the Coal Substance during Oxidation.—The examination of the samples withdrawn at each period during the oxidation included proximate analyses, of the usual type and by means of solvents, and ultimate analyses. The results are summarised in Tables II, III, and IV.

TABLE II.

Proximate Analyses. Oxidation at 100°.

		Original	Period I.	Period II.	Period III.	Period IV.
Vitrain	Moisture %	9·58	0·02	0·08	0·71	0·98
	Ash %	1·14	1·37	1·56	1·78	1·76
	Volatile matter (% on ash-free dry coal)	30·74	31·01	30·69	31·16	31·06
	Calorific value (cals. per g.)	7949	6969	6515	6348	6266
Durain	Moisture %	3·58	0·02	0·35	0·93	0·78
	Ash %	4·05	4·06	3·95	3·80	3·95
	Volatile matter (% on ash-free dry coal)	28·91	26·55	25·00	27·08	27·04
	Calorific value (cals. per g.)	7465	6973	6697	6530	6515
Fusain	Moisture %	1·66	0·10	0·32	0·92	0·90
	Ash %	17·78	17·57	17·76	17·80	17·96
	Volatile matter (% on ash-free dry coal)	19·84	23·69	22·27	20·98	20·78
	Calorific value (cals. per g.)	6466	5978	5891	5770	5750

The original moisture in the coals was driven off during the first period of oxidation and thereafter each ingredient showed an increasing tendency to retain water or to absorb it rapidly from the air, behaviour characteristic of coals that are naturally of high oxygen-content. The results of the "volatile matter" determinations indicate differences in the character of the oxidation of the different portions of the same seam of coal, the fusain and the durain presenting a peculiar contrast. The fusain showed an increase in the amount of volatile matter after the first period of oxidation, but the amount diminished as oxidation proceeded, assuming a nearly constant value higher than that of the original material; whilst with the durain there was a marked decrease at first and then a gradual increase to a constant value less than that of the original coal. With vitrain the values remained constant within the limits of experimental error, with perhaps a tendency towards a slight increase. The vitrain was the only one of the three

ingredients that coked strongly before oxidation and its coking-power was destroyed after the first period of heating. It will be noticed that the vitrain suffered the greatest depreciation in calorific value.

TABLE III.

Analyses by Solvents. Oxidation at 100°.

		Original.	Period I.	Period II.	Period III.	Period IV.
Vitrain	α-Compounds	79·7%	85·6%	85·4%	87·6%	87·6%
	β-Compounds	14·6	10·4	11·0	9·6	9·9
	γ-Compounds	5·7	4·0	3·6	2·8	2·5
	Ulmins	0·02	11·17	11·25	11·3	11·2
Durain	α-Compounds	90·5	90·0	90·0	87·9	87·6
	β-Compounds	6·8	7·05	—	9·2	9·4
	γ-Compounds	2·7	2·95	—	2·9	3·0
	Ulmins	0·01	2·6	5·58	6·6	6·52
Fusain	α-Compounds	95·2	95·20	96·54	95·0	94·15
	β-Compounds	3·4	3·35	—	3·5	4·45
	γ-Compounds	1·4	1·45	—	1·5	1·40
	Ulmins	nil	1·2	1·8	1·7	2·2

For convenience the nomenclature proposed by Stopes and Wheeler (" The Constitution of Coal," H.M. Stationery Office, 1918), which makes no presumptions as to the nature of the fractions obtained by means of solvents, has been employed, " α-compounds " signifying that portion of coal insoluble in pyridine at its boiling point, " β-compounds " that portion soluble in pyridine but insoluble in chloroform, and " γ-compounds " that portion soluble both in pyridine and chloroform.* The term " ulmins " signifies those compounds in the coal as a whole that were soluble in alcoholic potassium hydroxide.

The most striking changes on oxidation have occurred with the vitrain. Soluble ulmins were formed rapidly, the change by oxidation at 100° being apparently complete at the end of the first period of heating, and simultaneously about 30% of both the β- and γ-compounds (amounting to 6% of the coal) was destroyed. The β-compounds obtained from the original coal formed a chocolate-brown powder, whilst those from the oxidised coal appeared as brown nodules of dried jelly similar to the ulmins. It seemed probable, therefore, that the β-compounds from the oxidised vitrain contained a relatively large proportion of the ulmins. The quantities of material available from this series of experiments did not permit of testing this assumption directly, but it was found that the 87·6% of α-compounds only contained about half the ulmins produced.

* The α-, β-, and γ-compounds as thus defined are not necessarily similar in character in the oxidised and unoxidised coals.

The 9·9% of β-compounds recorded as being present in the oxidised coal must therefore be regarded as largely ulmified.

With both the durain and the fusain the changes on oxidation were not so great as with the vitrain, smaller amounts of ulmins were produced, and there was a tendency for the amounts of β-compounds (probably ulmified) to increase as oxidation proceeded.

TABLE IV.

Ultimate Analyses. Oxidation at 100°.

(Expressed as percentages on the ash-free dry substances.)

		Original.	Period I.	Period II.	Period III.	Period IV.
Vitrain	Carbon	79·7	74·3	72·2	71·9	72·1
	Hydrogen	5·2	4·1	3·9	3·8	3·8
	Oxygen	12·1	18·6	21·2	21·3	21·1
	Nitrogen	1·7	1·6	1·6	1·8	1·8
	Sulphur	1·3	1·4	1·1	1·2	1·2
Durain	Carbon	81·7	77·6	76·1	76·1	76·5
	Hydrogen	4·8	3·9	3·7	3·6	3·7
	Oxygen	11·3	16·3	17·8	17·8	17·1
	Nitrogen	1·6	1·4	1·4	1·4	1·5
	Sulphur	0·6	0·8	1·0	1·1	1·2
Fusain	Carbon	85·9	83·1	81·3	81·1	81·1
	Hydrogen	3·9	3·5	3·2	3·3	3·3
	Oxygen	8·4	11·6	13·6	14·1	13·8
	Nitrogen	1·3	1·2	1·3	1·0	1·2
	Sulphur	0·5	0·6	0·6	0·5	0·6

Analyses of α-Compounds.

		Original.	Period I.	Period II.	Period III.	Period IV.
Vitrain	Carbon	78·0	73·2	73·2	71·7	71·6
	Hydrogen	4·8	4·1	3·8	3·5	3·6
	Oxygen, etc.	17·2	22·7	23·0	24·8	24·8
Durain	Carbon	81·5	75·5	75·9	75·5	75·7
	Hydrogen	4·5	3·7	3·7	3·4	3·3
	Oxygen, etc.	14·0	20·8	20·4	21·1	21·0
Fusain	Carbon	86·9	83·5	82·2	81·4	81·2
	Hydrogen	3·8	3·4	3·2	3·1	3·2
	Oxygen, etc.	9·3	13·1	14·6	15·5	15·6

The vitrain, durain, and fusain from the original coal used showed the same gradations in analysis as were found by Tideswell and Wheeler for the Hamstead coal. During oxidation there was an increase of between 5 and 10% in the oxygen contents of each ingredient and a corresponding decrease in the carbon and hydrogen contents. With the vitrain, since the proportion of α-compounds increased markedly on oxidation, there was a tendency for their ultimate composition to approach that of the oxidised coal.

The proportions of nitrogen and sulphur did not vary outside the limits of experimental error, but the nature of the sulphur-

compounds present altered, as is shown by determinations of "sulphate" sulphur, as follows:

TABLE V.

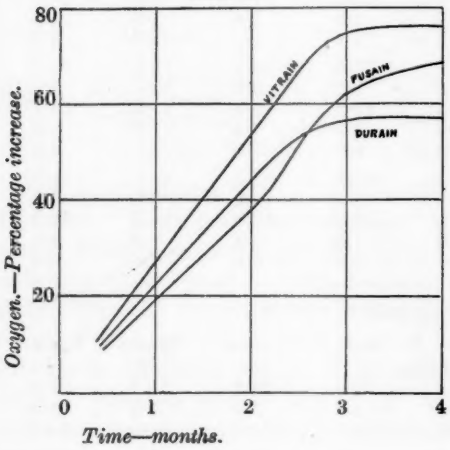
Sulphur as Sulphates. Per cent.

	Original.	Period I.	Period II.	Period III.	Period IV.
Vitrain	nil	0·18	0·15	0·15	0·14
Durain	,,	0·16	0·18	0·14	0·17
Fusain	,,	0·19	0·28	0·26	0·25

The sulphates were produced by the oxidation of pyrites originally present in the coal, the fusain being the ingredient that contained most pyrites.

A measure of the relative rates of oxidation of the three ingredients can be obtained from the percentage increase in the amount of oxygen present in the samples withdrawn at successive time-intervals. The results are shown in Fig. 1 as graphs which closely resemble those obtained in another manner by Tideswell and Wheeler for the rate of absorption of oxygen at 100° by vitrain, durain and fusain from Hamstead coal (J., 1920, **117**, 798, Fig. 3).

FIG. 1.



Oxidation at 150°.

It was assumed that at the end of 5 months' treatment the action of oxygen on the coals at 100° was complete, an assumption warranted by the analytical data so far as the vitrain is concerned, but perhaps not quite correct with respect to the durain, which as a whole was more resistant to attack. The remainder of each sample that had been oxidised at 100° during 5 months was now heated at 150° whilst moist air was drawn through. Heating was continued during 6 months, samples of the coals being withdrawn at intervals of 2 months and the liquids in the wash-bottles examined.

Liquid and Gaseous Products.—The wash-bottle connected to the fusain sample contained only a solution of carbon dioxide, but after each period of heating the solutions from the vitrain and durain samples were markedly acid (sulphurous acid) and contained

formaldehyde. The presence of acetone or methyl alcohol could not be detected.

Changes in Weight.—During oxidation at 100° the weight of each coal had at first increased slightly and then decreased, the final values being: vitrain + 0·8, durain — 1·3, and fusain — 1·4% on the original weight. Oxidation at 150° resulted in a progressive decrease in weight, as is shown in Table V.

TABLE V.

Loss in weight on oxidation at 150°. Per cent.

	Period I.	Period II.	Period III.	Total.
Vitrain	8·8	7·3	0·2	16·3
Durain	4·6	5·5	3·0	13·1
Fusain	3·3	4·4	0·8	8·5

Changes in the Coal Substance.—The changes that took place in the character of the coals during oxidation at 150° are best appreciated by comparing the analytical data with those recorded for the final samples oxidised at 100°. Each coal showed a marked increase in the amount of " volatile matter " and an increase in ash-content occasioned by the loss in weight of combustible matter. These results are recorded in Table VI.

TABLE VI.

Proximate Analyses. Oxidation at 150°.

		Final oxidation at 100°.	Period I.	Period II.	Period III.
Volatile matter % on ash-free dry substance	Vitrain	31·0	40·7	40·4	40·5
	Durain	27·0	31·8	32·1	32·2
	Fusain	20·8	25·9	25·9	27·1
Ash %	Vitrain	1·76	2·22	2·15	2·17
	Durain	3·95	4·73	4·86	4·95
	Fusain	17·96	17·98	17·90	18·25

The most remarkable result of the oxidation at 150° was that the vitrain was rendered nearly completely soluble in alcoholic potassium hydroxide (compare Charpy and Decorps, *Compt. rend.*, 1921, 175, 807), whilst the durain and fusain also contained greatly increased quantities of ulmins. The quantities, together with the results of analysis by means of pyridine and chloroform, are recorded in Table VII.

It has been seen that oxidation at 100° tended to destroy the compounds soluble in pyridine, and to a less degree those soluble both in pyridine and chloroform. Further oxidation at 150° apparently destroyed the γ-compounds completely, or at all events rendered them insoluble in chloroform; at the same time larger

TABLE VII.

Analyses by Solvents. Oxidation at 150°.

		Final oxidation.	Period I.	Period II.	Period III.
Vitrain	α-Compounds	87·6	75·9	57·7	55·0
	β-Compounds	9·9	23·2	42·3	45·0
	γ-Compounds	2·5	0·9	trace	nil
	Ulmins	11·2	93·5	97·0	95·5
Durain	α-Compounds	87·6	87·4	80·3	77·0
	β-Compounds	9·4	12·1	19·7	23·0
	γ-Compounds	3·0	0·5	trace	nil
	Ulmins	6·5	36·1	43·5	46·0
Fusain	α-Compounds	94·2	94·5	82·0	80·0
	β-Compounds	4·5	5·5	18·0	20·0
	γ-Compounds	1·3	trace	trace	nil
	Ulmins	2·2	14·2	19·5	24·0

proportions of the coals were rendered soluble in pyridine. It is doubtful, however, whether with these oxidised coals the degree of solubility in pyridine is of much significance, since prolonged exposure of the coals to pyridine results in further extraction.

TABLE VIII.

Ultimate Analyses. Oxidation at 150°.

(Expressed as percentages on the ash-free dry substances.)

		Final oxidation at 100°.	Period I.	Period II.	Period III.
Vitrain	Carbon	72·1	66·4	64·7	64·9
	Hydrogen	3·8	2·7	2·5	2·3
	Oxygen, etc.	24·1	30·9	32·8	32·8
Durain	Carbon	76·5	71·9	68·9	67·0
	Hydrogen	3·7	2·5	2·6	2·3
	Oxygen, etc.	19·8	25·6	28·5	30·7
Fusain	Carbon	81·1	77·8	73·9	74·2
	Hydrogen	3·3	2·4	2·3	2·2
	Oxygen, etc.	15·6	19·8	23·8	23·6
	Analyses of α-Compounds.				
Vitrain	Carbon	71·6	67·7	65·9	64·9
	Hydrogen	3·6	3·1	2·7	2·3
	Oxygen, etc.	24·8	29·2	31·4	32·8
Durain	Carbon	75·7	73·1	69·9	—
	Hydrogen	3·3	2·8	2·9	—
	Oxygen, etc.	21·0	24·1	27·2	—
Fusain	Carbon	81·2	78·2	77·0	75·2
	Hydrogen	3·2	2·5	2·5	2·3
	Oxygen, etc.	15·6	19·3	20·5	22·5

Ultimate analyses were also made of some of the samples of ulmins produced on oxidation at 150°, as follows :

		Carbon.	Hydrogen.	Oxygen, etc.
From vitrain.	Period I.	64·8	2·8	32·4
From vitrain.	Period II.	64·5	2·7	32·8
From vitrain.	Period III.	64·6	2·6	32·8
From durain.	Period III.	65·4	3·0	31·6

All these ulmins have similar analyses and the similarity extends to ulmins produced from the coals by oxidants other than air, to which reference will be made later. With vitrain, which was completely ulmified by oxidation at 150°, the analysis of the coal as a whole and that of the α-compounds contained in it were also similar. Thirty or more analyses of the fully oxidised vitrain have shown between 62 and 66% of carbon and between 2·6 and 3·5% of hydrogen. Some of these observed slight differences in analysis may be accounted for by the fact that the ulmins are unstable compounds and suffer slight decomposition, with elimination of water, on prolonged heating at 150°.

It is apparent that marked changes have taken place in the coals during oxidation at 150°. With vitrain, almost the whole of the coal substance has been converted into alkali-soluble ulmins, whilst large proportions of both the durain and the fusain have been so converted. It is to this ulmin formation that the changes in the proximate and ultimate analyses, and in the general character of the coals, are due. The ultimate analyses show that the carbon content of the vitrain reached a minimum value owing to its almost complete conversion into alkali-soluble ulmins, whilst the corresponding values for the durain and the fusain are higher because of the presence of substances more resistant to such ulmification or perhaps incapable of it.

Oxidation at 200°.

Oxidation was continued at a higher temperature to find out whether complete ulmification of the durain and fusian would occur and to determine what changes, if any, would take place in the vitrain. The remaining portions of the samples heated at 150° were oxidised at 200° during 1 month and examined. Each ingredient had lost about 25% in weight during this treatment, with a corresponding increase in its percentage of ash. A final period of oxidation during a fortnight was then carried out. Analytical data are recorded in Table IX.

Further ulmification of the durain had occurred, but was by no means complete, nor did it appear that more prolonged heating, or heating at a higher temperature, would be satisfactory, for decomposition of the oxygenated coals (with the production of carbon dioxide and carbon monoxide) was taking place fairly rapidly. The ulmins produced from the vitrain at 150° began to decompose (as is shown by the ultimate analyses) and were rendered partly

TABLE IX.

Oxidation at 200°.

	Vitrain.		Durain.		Fusain.	
	Period I.	Period II.	Period I.	Period II.	Period I.	Period II.
Loss in weight %	27·0	7·2	23·5	7·4	19·7	7·0
Ash %	2·8	2·8	6·4	6·5	21·4	21·5
Volatile matter (% on ash-free dry substance)	38·5	39·0	37·8	37·1	29·8	31·2
Ulmins	70·0	75·0	64·0	65·0	20·5	22·0
Soluble in pyridine	28·0	30·0	22·0	24·0	11·0	13·0
Carbon (% on ash-free dry substance)	65·8	65·9	69·8	70·0	72·8	71·3
Hydrogen (% on ash-free dry substance)	2·0	2·01	1·8	1·76	1·8	1·6
Oxygen, etc. (% on ash-free dry substance)	32·2	32·09	28·4	28·24	25·4	27·1

insoluble in alcoholic potassium hydroxide; indeed the solutions obtained were unlike those of the true ulmins, being turbid and lacking the rich brown colour. So far as the vitrain is concerned, the production of alkali-soluble ulmins must be regarded as having been completed by oxidation at 150°.

By carefully regulated oxidation it has thus been found possible to obtain from all the ingredients of the coal examined ulmins having similar analyses and properties and presumably derived from substances of the same nature that occur in different proportions in each ingredient. The vitrain consists almost entirely of these "reactive" compounds, the durain contains a certain proportion of relatively "inert" substances, and the fusain a greater proportion.

These conclusions bear out and amplify the suggestion made by Tideswell and Wheeler (*loc. cit.*, p. 633) that the difference, chemically, between the vitrain, clarain, durain and fusain of a banded bituminous coal lies in the proportion of relatively "inert" or unresponsive material with which the "reactive" portion is associated, the "reactive" group of compounds being of the same chemical nature in each ingredient and containing more oxygen and less carbon than the "inert" material, which may differ in character as between one ingredient and another. The present research specifies as the "reactive" group of compounds those that can be converted by oxidation into alkali-soluble ulmins. The "inert" substances are those that remain after a durain or a clarain has suffered all the ulmification possible by oxidation, and it would appear that they impart to the coal most of the specific qualities it may possess. For examination of the residue from the durain after ulmification had been completed showed that it consisted essentially of the plant entities (chiefly spore-exines) that, originally resistant to the processes (bacterial and other) that resulted in the formation of the coal conglomerate, still remained resistant to oxidation.

This process of formation of alkali-soluble ulmins by oxidation (more properly, a process of regeneration) thus affords means, which we have long sought, of effecting a separation of the different plant entities from the coal mass and examining their chemical properties, according to the scheme outlined by Stopes and Wheeler ("The Constitution of Coal," H.M. Stationery Office, p. 41). The process of oxidation by air at 150° is a long one and only admits of the treatment of small quantities of coal. We therefore made comparative experiments with other oxidants the action of which could be regulated and found in hydrogen peroxide a reagent which, if carefully used, would rapidly effect the complete transformation of a vitrain into alkali-soluble ulmins and, whilst rendering the bulk of a clarain or a durain soluble, would leave their characteristic plant tissues substantially unaltered. The analysis of ulmins prepared by the action of hydrogen peroxide on coal averages: carbon 64·3, hydrogen 3·5, and oxygen 31·2%, which is in close agreement with that of the similar compounds produced by slow atmospheric oxidation at 150°.

We have spoken of the formation of alkali-soluble ulmins from bituminous coal as a "regeneration." The solubility of the ulmin-compounds in alkaline solutions to form dark brown liquors is usually regarded as one of their chief characteristics and this property is used for their estimation. From estimations made in this way it is found that the various groups of alkali-soluble ulmin-compounds form a large proportion of the "humus" of decayed wood; they occur, sometimes in considerable quantities, in peats; lignites also contain them, but in normal bituminous coals they occur rarely, and then only in minute quantities, whilst in anthracites their presence has never been detected. In other words, the further the natural "carbonisation" of the fuel has progressed the smaller is its content of soluble ulmins. From this it is probable that the ulmin compounds once formed during the early processes of formation of the fuels have been subsequently so modified as to render them unrecognisable by their solubility in alkalis. Berthelot and André (*Ann. Chim. Phys.*, 1892, (vi], **25**, 420) observed that both ulmins formed artificially from sugar and those occurring naturally in soil began to decompose on exposure to air when moist, carbon dioxide being evolved; Roger and Vulquin (*Compt. rend.*, 1908, **147**, 1404) made a similar observation on peat ulmins and noted also that they became insoluble in alkalis; whilst Tideswell and Wheeler have recorded in their study of dopplerite (J., 1922, **121**, 2345) that this undoubted ulmin is less readily soluble in alkalis than that in more recent peats. Solubility in alkalis to form brown solutions should not, therefore, be regarded as a necessary property of the

ulmins, but it must be recognised that they can (through polymerisation and dehydration) change in character so as to lose their "characteristic" solubility.

Neither the insoluble ulmins, which we consider form the major part of newly-won bituminous coals, nor the soluble ulmins regenerated from them by oxidation are identical in character with those that form the major part of peat, but they possess the same nuclear structure. The external groupings of the ulmin molecules in unoxidised coal are modified during oxidation, the more easily detached groupings being eliminated to form simple oxygenated compounds, whilst the residual ulmin becomes more definitely of acidic character (more so than the peat ulmins) owing to the formation of carboxylic groupings in place of those detached. Pearson (*Fuel*, 1924, **3**, 297) has reached similar conclusions to these as the result of his work on the oxidation of coals by sulphuric acid and bromine, although the analyses of the ulmins so formed differ from ours (obtained either by atmospheric oxidation or by the use of hydrogen peroxide), no doubt because chemical changes other than oxidation occurred during his experiments.

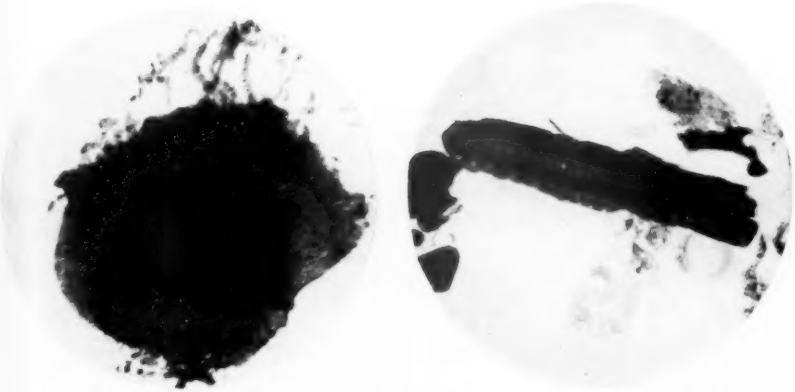
Bituminous coal, then, consists essentially of insoluble ulmins in which morphologically organised plant tissues (that have escaped ulmification) are dispersed.* The present work shows that alkali-soluble ulmins can be regenerated from a bituminous coal by mild oxidation. If the coal is a vitrain, it consists almost solely of ulmins; whilst the regeneration of alkali-soluble ulmins in a clarain, a durain, or a fusain leaves residues, characteristic of each of those ingredients, which are essentially the original plant entities that were particularly resistant to, or were preserved from, the processes of "decay" that constituted the early stages of coal-formation, and are, apparently, but little altered.

The character of these residues is illustrated in Fig. 2, in which (*a*) and (*b*) are photomicrographs of cuticular tissues such as can be separated from a clarain by treatment with hydrogen peroxide and alcoholic potassium hydroxide, (*c*) shows the exine of a megaspore, characteristic of the *débris* from a durain, obtained in the same manner, and (*d*) a wood tracheid such as occurs in the *débris* of a fusain. Future communications will deal with the chemical

* For the sake of simplicity, we have here omitted discussion of the presence of natural plant-substances devoid of morphological organisation, such as "resin," in the coal conglomerate. We have evidence that these resist oxidation at low temperatures and appear amongst the plant *débris* after the process of regeneration of alkali-soluble ulmins by means of hydrogen peroxide (or atmospheric oxidation). This work will be described in a forthcoming publication which deals also with the chemical properties of the regenerated ulmins.

FIG. 2.

(*a*) and (*b*). Fragments of cuticular tissue, characteristic plant entities in a clarain. (*a* × 30 and *b* × 180.)



(*c*) and (*d*). The exine of a megaspore (× 30) and a wood tracheid (× 250), characteristic plant entities in a durain and a fusain respectively.

[*To face Trans., p.* 124]

examination of similar plant-tissues separated in bulk from coal; in particular with cuticles and spore-exines, since these are so often the predominant structures to be found in clarains and durains, respectively, and most bituminous coals consist mainly of clarain and durain. Work on modern cuticles and spore-exines, for comparison, has already been in progress some years in the belief, now justified, that it should be possible to isolate individual tissues or identifiable parts from coal so that, for example, any characteristic distillation products of which they are the source can be determined.

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SHEFFIELD UNIVERSITY. [*Received, September 20th*, 1924.]

XXI.—*On Fusain and its Oxidation. Studies in the Composition of Coal.*

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER.

SPONTANEOUS combustion in a seam of coal, in so far as it may be determined by the chemical composition of the materials composing the seam, originates with the most readily oxidisable ingredient thereof. Amongst mining men there is a belief, the history of which it is unnecessary to trace, that a frequent cause of spontaneous combustion is the presence in the seam of fusain; * that fire actually originates in bands of fusain, when such are present, and travels preferentially along them.

Data regarding the rate of oxidation of a fusain have been supplied by Winmill (*Trans. Inst. Min. Eng.*, 1913, **46**, 563), who concluded that of all parts of the Barnsley seam, which he examined in detail, the fusain was the least capable of heating spontaneously. Our own experiments when using coal from the Hamstead Thick seam (J., 1920, **117**, 794) gave quite different results. The vitrain, clarain and durain (the brilliant, bright and dull portions of the seam) absorbed oxygen at rates graded in the direction expected from previous work on the chemical constitution of these ingredients of banded bituminous coal (J., 1919, **115**, 619), but the fusain stood apart. At 15° and 50° its absorptive power for oxygen was several times greater than that of the rest of the coal, although at 100° it was of the same order. From this it can be concluded that the fusain, weight for weight, is the most liable to self-heat (from

* Sometimes called "mother of coal," "mineral charcoal," "dant," or "sooty partings."

atmospheric temperature) of all the ingredients of the Hamstead coal. It would not, however, be justifiable to assume that fusains from other coals behave similarly—Winmill's work, indeed, suggests that they do not—and further experiments with a number of samples of fusain and of the coals associated with them were therefore undertaken.

During the progress of this work, which was begun in 1919, determinations of the rates of oxidation of a number of fusains from different coal-fields have been published by Graham (*Trans. Inst. Min. Eng.*, 1923, **66**, 41), who has summarised his results as follows: "This ingredient of coal may vary very considerably in composition, but such variation does not appear, at low temperatures, to affect materially the absorption of oxygen which in all cases is considerably smaller than that shown by a bituminous coal liable to spontaneous combustion. In general, from the chemical point of view fusain may be exonerated from being considered as the source of the main production of heat during the initial stages of most cases of spontaneous combustion."

The following results may be quoted from Graham's work, the oxygen absorbed being expressed in c.c. at *N.T.P.* per gram of fusain:

Fusain description.	Oxygen absorbed from air at 30° during 96 hours. C.c.
Mossfield seam (North Staffs.)	1·93
Seven Foot seam (North Staffs.) (*a*) Soft variety	1·19
Seven Foot seam (North Staffs.) (*b*) Hard variety	2·04
South Wales (*a*) Soft variety	1·87
South Wales (*b*) Hard variety	1·61

The absorption of oxygen by the actual coals with which the fusains were associated was not measured, but Graham compared his results with some obtained by Winmill (*ibid.*, 1916, **51**, 493), under similar conditions of experiment, for coals "liable to spontaneous combustion," the values for which lay between 3·0 and 6·0 c.c. A closer scrutiny of Winmill's figures shows, however, that coal from the same fields as those from which Graham's fusains were obtained did not absorb oxygen any more readily, and Graham's generalisation does not seem to us justifiable on the evidence.

We have measured the absorption of oxygen of a number of coals and of the fusains actually associated with each, and we cannot agree that fusains in general absorb oxygen at slower rates than do coals liable to spontaneous combustion.

Seventeen samples of fusain, with samples of the adjoining coals, were collected for us by H.M. Inspectors of Mines and from these four were chosen, according to their apparent purity, for oxidation tests.

The samples were as follows:—

Lab. No. A. From Top Hards, Barnsley Seam, Hucknall No. 2 Pit, Notts.

Lab. No. B. From Robin's Seam, Cannock Old Coppice Colliery, Walsall, Staffs.

Lab. No. C. From Deep Softs Seam, Mapperley Colliery, Notts.

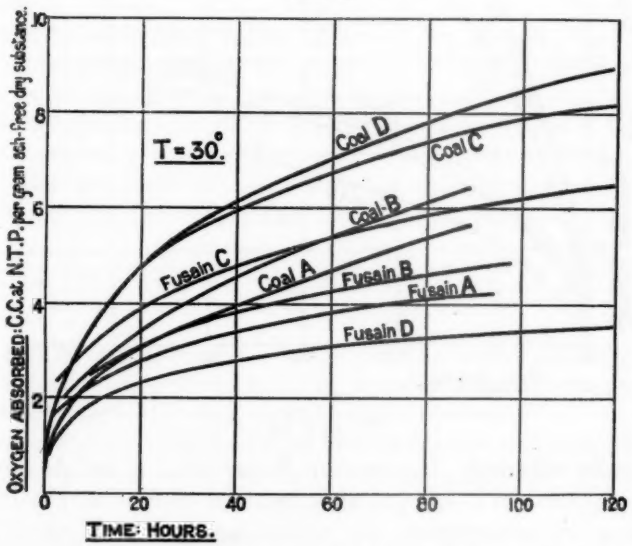
Lab. No. D. From Dysart Main Colliery, Fife.

Analytical data respecting these samples are given in Table I.

TABLE I.

	A.		B.		C.		D.	
	Fusain.	Coal.	Fusain.	Coal.	Fusain.	Coal.	Fusain.	Coal.
Moisture, per cent. ...	5·6	9·4	5·6	8·9	2·6	9·8	5·7	10·9
Volatile matter (other than moisture) ...	15·7	39·0	17·1	39·8	13·0	40·4	12·3	35·9
Ash	10·3	3·3	14·7	8·3	12·5	7·7	11·8	1·3
Carbon, per cent. (on ash-free dry coal)	89·4	79·1	79·8	73·5	87·5	75·6	84·6	78·5
Hydrogen	3·0	5·0	3·3	4·8	3·0	4·7	3·2	4·6
Oxygen	7·0	12·8	6·1	15·3	6·4	16·5	10·5	15·1
Nitrogen	0·4	2·2	0·4	1·5	0·7	1·9	0·4	1·3
Sulphur	0·2	0·9	10·4	4·9	2·4	1·3	1·3	0·5

FIG. 1.



The method of experiment was to circulate oxygen in a closed system through the coal or fusain packed in a tube maintained at a constant temperature.* The absorption of oxygen was calculated

* Details of the apparatus used and of the method of experiment are given in J., 1920, **117**, 795, whilst a diagram of a similar apparatus is shown in J., 1912, **101**, 831.

from the reduction of pressure. Before and after oxidation at a given temperature, each sample was heated in a vacuum at 200°. The results obtained are shown diagrammatically in Figs. 1 and 2 and are summarised in Tables II and III.

These results cannot be directly compared with those of Graham, for he used air in his experiments, but Winmill has found (*Trans. Inst. Min. Eng.*, 1916, **51**, 493) that the absorption of oxygen by coal is nearly proportional to the square root of its concentration,

FIG. 2.

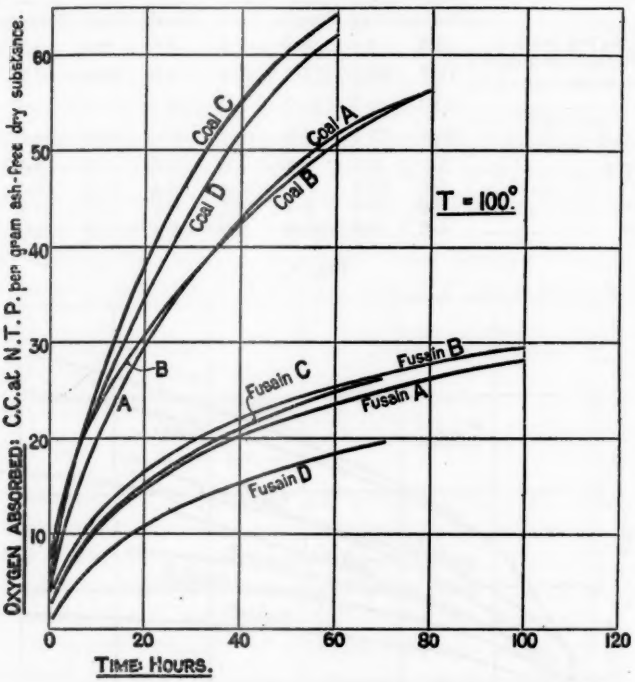


TABLE II.

Oxygen absorbed. C.c. at N.T.P. per gram of ash-free dry substance.

Temp.	Time (hours).	Sample. A. Fusain.	A. Coal.	B. Fusain.	B. Coal.	C. Fusain.	C. Coal.	D. Fusain.	D. Coal.
30°	1	1·3	1·0	1·4	1·2	1·8	1·5	0·8	1·4
	10	2·3	2·4	2·5	2·6	3·2	3·8	1·8	3·8
	50	3·5	4·3	4·0	5·0	5·1	6·4	2·9	6·7
	96	4·3	5·8	4·8	6·6	6·2	8·1	3·5	8·5
100°	10	10·5	19·2	12·2	22·4	11·0	25·0	7·2	23·8
	50	22·0	48·0	24·0	47·0	22·8	61·0	17·0	59·0

TABLE III.

Ratio: Oxygen absorbed by fusain : Oxygen absorbed by coal.

Temp.	Time (hours).	Sample. A.	B.	C.	D.
30°	1	1·3	1·2	1·2	0·6
	10	0·95	0·96	0·84	0·47
	50	0·83	0·81	0·80	0·43
	96	0·74	0·73	0·76	0·41
100°	10	0·55	0·55	0·44	0·30
	50	0·46	0·48	0·38	0·28

so that a rough comparison can be made if Graham's figures are doubled. It then appears that the fusains he used were decidedly less readily oxidised at 30° than most of those we have investigated. We suggest that this is due in part to the different experimental methods used (Graham, for example, does not appear to have allowed for the oxidation of his samples at atmospheric temperature previous to their introduction into his apparatus), but mainly to differences in the nature of the fusains themselves. The abnormally low rate of oxidation of the Barnsley fusain recorded by Winmill would appear to be due to weathering of the sample previous to his tests.

It will be seen from Tables II and III that with three of the pairs of samples examined the initial absorption of oxygen by the fusain at 30° was greater than that by the coal, but on comparing the results obtained at 30° and 100°, the oxidisability of fusain is found to increase less rapidly with temperature than that of the coal. The temperature coefficients of the amounts of oxygen absorbed during the early stages (up to 10 hours) are :

	A.	B.	C.	D.	Hamstead.
Fusain	1·24	1·27	1·12	1·29	1·20
Coal	1·34	1·34	1·39	1·37	1·35

In each instance the coefficient is less than 2 and probably is the resultant of two coefficients. The reaction between oxygen and coal is not simple : it may be expressed as follows :
Coal and oxygen $\longrightarrow$ coal-oxygen (adsorbed) $\longrightarrow$ coal-oxygen (complex) $\longrightarrow$ oxidised coal + oxides of carbon + water.

The last phase of the reaction is incomplete at low temperatures, but can be completed by raising the temperature (it is nearly complete at 200°); at such low temperatures absorption of oxygen is determined by the formation of the coal-oxygen complex. Compared with the rate of formation of this complex, the first action of adsorption may be regarded as instantaneous. The rate of complex formation will therefore depend on the concentration of oxygen on the surface of the coal. The temperature coefficient of the con-

centration of adsorbed oxygen on the surface of the coal is less than unity and is probably about 0·80 (see Graham, *Trans. Inst. Min. Eng.*, 1916, **52**, 338; Tideswell and Wheeler, J., 1919, **115**, 895). Assuming that the rate at which the coal-oxygen complex is formed is directly proportional to the concentration of the oxygen maintained on the surface of the coal and that its temperature coefficient is 2, the expected coefficient for the series of reactions would be 1·6. The observed values are less. An explanation of this is that the surface of the coal becomes clogged by the products of decomposition of the complex, an effect which would be greater the higher the temperature of reaction and more noticeable with fusain than with coal because of the more open texture of its surface.

A study of the gases evolved during the oxidations (see Table IV) suggests that the mode of oxidation of fusain and of coal is similar. At 30° the amount of carbon monoxide was too small to admit of exact determination, but at 100° the volumes were both larger and more regular in amount and it was found that the ratio between the carbon dioxide and carbon monoxide produced at this temperature lay within the same range (2·4 to 3·4) with the fusains as with the coals.

TABLE IV.

Oxides of carbon evolved. Per cent. of oxygen absorbed.

Temp.			Sample. A.	B.	C.	D.
30°	Carbon dioxide	Fusain	4·0	0·8	1·6	0·8
		Coal	1·5	3·2	5·6	0·7
100	Carbon dioxide	Fusain	12·8	11·7	10·8	14·5
		Coal	10·6	12·1	14·5	17·6
100	Carbon monoxide	Fusain	4·7	4·0	4·0	4·4
		Coal	4·0	4·9	6·2	5·2
	Ratio $\frac{CO_2}{CO}$	Fusain	2·7	2·9	2·7	3·3
		Coal	2·65	2·5	2·4	3·4

With none of the fusains examined was the rate of absorption of oxygen at low temperatures so rapid as with the Hamstead fusain, which may be regarded as exceptional. Fusain does not form an important part by weight (rarely more than 5%) of the mass of a coal, but it occurs frequently in patches or in layers of considerable extent, generally adjacent to or embedded in bright coal, and its porous nature allows of ready access of oxygen. Both its chemical properties and its physical state therefore enable it to produce the first local rise in temperature that may result in self-heating of the adjacent coal. Once the temperature has risen, the continuance of the heating is no doubt mainly due to oxidation of the coal.

It is not to be expected that all fusains, no matter from what seams of coal they are procured, should have similar chemical and physical properties, any more than that all coals should be similar.

We have, in fact, evidence from the work of Sinnatt (*Trans. Inst. Min. Eng.*, 1921, **62**, 156) that in the Lancashire coal-fields there are at least two types, a dense and a pulverulent variety, whilst, as already mentioned, the Hamstead fusain with which we made our previous experiments seems to be of a particularly reactive character. We concluded from our work on banded bituminous coal (*loc. cit.*, p. 634) that the three principal ingredients of Hamstead coal, vitrain, clarain and durain, are each composed of a " reactive " group of compounds together with a relatively " inert " material, and differ from one another mainly in the proportions of these constituents contained in them. Although the fact was not emphasised at the time, the chemical examination of the Hamstead fusain showed that it also must be regarded as containing a certain proportion of " reactive " constituents, of similar type to those in the coal, which is responsible for many of its properties. Similarly, it would appear from Sinnatt's work and from our own observations that many, if not all, fusains consist of an intimate mixture of coaly material with an " inert," or true fusain, constituent.

The occurrence of fusain in coal seams is usually attributed to rapid aerial decay of the plants at or near the water surface of the swamps in which most of the *débris* was submerged, and the process most often appears to have taken effect on the woody parts of the plants. There is no reason why such aerial decomposition should always have been completed before the plants became submerged and anaerobic decomposition began; indeed it is more probable that in the majority of instances the aerial decay was not complete. Fusains may therefore be expected to differ from one another not only, occasionally, by reason of differences in the plant remains fusainised, but also, frequently, because the material has suffered in differing degree an in part aerobic and in part anaerobic decomposition, the latter resulting in ulmification. Lomax has, indeed, observed complete stems of plants that have been fusainised on the outside and consist of true coal within (*Trans. Inst. Min. Eng.*, 1921, **62**, 171), but we suggest that each individual fusain fibre may often consist of an inner core of coaly material with an outer layer of true fusain, with, no doubt, intermediate zones merging the one into the other; and there may also be only partial fusainisation of some of the cell-walls composing the fibre.

The " true fusain " material appears to be quite insoluble in organic solvents; it yields mainly oxides of carbon and methane on distillation, with little or no liquid products, and consists usually of thickened and " carbonised " cell-walls. We consider that the intimate admixture of different proportions of oxidisable coaly material with this chemically " inert " but very porous true fusain

material mainly determines the different degrees of oxidisability of fusains as they exist in coal, the fusain in the Hamstead coal, for example, containing a high proportion of coaly material throughout its fibres. Support is lent to this view by analyses of a number of fusains made for us by Mr. A. E. Beet. These samples of fusain had been collected with great care and before they were subjected to analysis were examined closely for fragments of adhering coal. Yet it was found that each could be separated into two distinct classes of material by sieving through a 40's mesh. The fraction which remained on the sieve was associated with much coaly material, to judge by the results of analysis (more particularly distillation tests at 900°), though it could not be recognised as coal; whilst that which passed through was, on the same evidence, mainly what we have termed " true fusain " material.

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XXII.—*The Chemistry of Lignin. Part II. A Comparison of Lignins Derived from Various Woods.*

By WALTER JAMES POWELL and HENRY WHITTAKER.

IN Part I of this series (J., 1924, **125**, 357), the preparation and properties of lignin derived from flax shoves and of several of its derivatives were described. The chief conclusions drawn were that the empirical formula for flax lignin which agrees most closely with all the analytical data is $C_{45}H_{48}O_{16}$, and that the molecule contains one active aldehyde group and nine hydroxyl groups, of which four are methylated. The investigation has now been extended on the same lines to lignins obtained from a number of woods, and poplar, birch, ash, spruce, larch and pine lignins, together with some derivatives of these substances, have been examined. The wood lignins were isolated in the same way as flax lignin, the wood in the form of small chips being digested for 6 to 10 hours under pressure at temperatures varying from 140° to 160° with caustic soda solution, the strength of which varied from 8 to 12%. The black liquor was drained from the cellulose and treated while still hot with a slight excess of hydrochloric acid, the precipitated lignin being washed by decantation with hot dilute hydrochloric acid, centrifuged and dried. An objection might be raised that this method of isolation would cause internal changes to take place in the lignin molecule. Lignosulphonic acid, however,

has been obtained from spruce wood by Dorée and Hall (*J. Soc. Chem. Ind.*, 1924, **43**, 257T) by a mild process—the action of a 7% solution of sulphurous acid at 100—110°—and the composition of this substance corresponds with the formula $C_{26}H_{30}O_{12}S$, from which the formula $C_{26}H_{28}O_9$ for lignin is obtained. This requires C = 64·4, H = 5·9%; and these figures are in close agreement with our results (Table I). Our product is therefore not more highly condensed than that of Dorée and Hall, and both are probably closely related to lignin as it exists in the lignocellulose complex.

The crude lignin was purified by pouring the solution in aqueous acetone into a large volume of hot 20% hydrochloric acid, the precipitate being collected and thoroughly washed with hot water.

The results now obtained show conclusively that the lignins from the different natural sources so far examined are derivatives of the same hydroxy-compound, and that they differ only in the number of methoxyl groups which they contain. This difference is mainly due to the fact that the methoxyl content of lignin in wood varies from one species to another, while in any one species variations occur according to the age of the tree. In addition, the methoxyl content of lignin isolated in the manner already described is affected by the strength of caustic soda solution and the time and temperature of digestion. Lignin as isolated is therefore a mixture of methylated derivatives of a polyhydroxy-compound, and it should be possible by chemical means to effect separation into fractions of definite methoxyl content, but our attempts to do so have not yet met with success. The separate fractions obtained by precipitating lignin from its solution in caustic soda by addition of hydrochloric acid gave the same figures on analysis.

In deducing the formula $C_{45}H_{48}O_{16}$ from the analytical results given by flax lignin and its derivatives, the assumption was made that the molecule contained a definite number of methoxyl groups, whereas in our present view there is no reason to suppose that such is the case. Instead of the total of nine hydroxyl groups indicated by analysis of acetyl-lignin, it is possible to suggest formulæ containing eight or ten hydroxyl groups (*e.g.*, $C_{40}H_{44}O_{14}$) which agree equally well with the analytical data. At this stage of the work, however, it is not desirable to make a decision in favour of one or the other of these formulæ and until more data are available we intend to continue using the formula adopted for flax lignin, $C_{45}H_{48}O_{16}$.

From the six wood lignins, purified as described above, the acetyl compounds were prepared by treatment on the steam-bath with acetic anhydride and sulphuric acid. The acetyl content varied according to the methoxyl content, but in each case, using the

empirical formula $C_{45}H_{48}O_{16}$ as the basis of calculation, the total of acetylated and methylated hydroxyl groups was nine, although the actual number of methylated groups varied between three and five. All the acetyl compounds were insoluble in cold alkali and it is therefore unlikely that there are any carboxyl groups in the molecule. The variations in methoxyl content of the various wood lignins prepared were not sufficient to affect the determinations of carbon and hydrogen which were carried out on the purified samples, and the figures obtained were constant within the limits of experimental error. Table I gives a summary of the analytical results and also the number of groups calculated on the basis of the formula $C_{41}H_{40}O_{16}$ for the parent hydroxyl compound itself. It is proposed to assign the name *lignol* to this compound.

TABLE I.

Substance analysed.	Determination.	Source of Lignin. Flax.	Larch.	Pine.	Spruce.	Ash.	Birch.	Poplar.
Lignin.	C	63·9	63·8	63·4	64·0	63·2	63·2	63·3
	H	5·8	5·2	5·6	5·5	5·6	5·5	5·8
	CHO	3·1	—	2·9	3·1	—	3·2	—
Acetyl-lignin.	OMe	11·8	9·0	11·5	11·0	13·3	15·2	12·6
	$CO{\cdot}CH_3$	20·5	23·0	18·9	19·4	17·6	14·5	17·5
No. of OMe groups.		4·0	3·1	3·9	3·8	4·5	5·0	4·3
No. of $CO{\cdot}CH_3$ groups.		5·0	5·8	4·5	4·8	4·3	3·4	4·3
Total groups.		9·0	8·9	8·4	8·6	8·8	8·4	8·6
Acetylmethyl-lignin	OMe	20·3	19·9	20·4	23·1	20·0	22·4	22·7
	$CO{\cdot}CH_3$	11·1	11·8	10·5	8·0	11·3	8·1	7·5
No. of OMe groups.		6·5	6·4	6·5	7·2	6·4	7·0	7·0
No. of $CO{\cdot}CH_3$ groups.		2·6	2·7	2·4	1·8	2·6	1·8	1·7
Total groups.		9·1	9·1	8·9	9·0	9·0	8·8	8·7

The table shows that lignol from each of the wood lignins examined has the same empirical formula and the same number of hydroxyl groups as that from flax lignin. In order to verify this statement experimentally, attempts have been made to isolate lignol from the various lignins by the action of hydriodic acid. However, on treating lignin with hydriodic acid (*d* 1·7) at 130°, a dark brown product, which appeared to be a mixture, was obtained. The main fraction of this product was insoluble in caustic soda and cannot therefore be lignol, and as the percentage of carbon found is much higher than that calculated, it appears that reduction takes place during the reaction with hydriodic acid.

Confirmation of the results and conclusions drawn from the analysis of the acetylated lignins was obtained by examination of the methylated derivatives. The latter were prepared by treatment of the sodium hydroxide solution of lignin with methyl sulphate in the cold. It is not possible to methylate more than seven of the hydroxyl groups under the conditions employed, and

in some cases full methylation was obtained only after several treatments. The product from a single treatment, however, after being washed with dilute sodium hydroxide solution, was acetylated in the usual manner, and the total of methoxyl and acetyl groups in all the products was found to be practically constant. It was stated in the paper on flax lignin (*loc. cit.*) that the proportion of acetyl in acetylmethyl-lignin was too low to account for the presence of two acetyl groups. In the experiments on which this statement was based, acetic anhydride alone was used as the acetylating agent, but it has since been found that in presence of sulphuric acid the diacetyl derivative is readily formed. The analytical data given in Table I for the acetylmethyl-lignins strongly support the view that all the various lignins examined have the same empirical composition and number of hydroxyl groups in the molecule.

Derivatives of an entirely different character from those already described result when lignin is treated with chlorine or bromine, and if there were any fundamental differences in the molecular structure of the various lignins, it is unlikely that the same halogenated derivative would be obtained in each case. In our study of flax lignin we found that the chlorination or bromination product contained twelve halogen atoms, and that a large quantity of hydrogen chloride or bromide was evolved during halogenation. Most of the methoxyl groups originally present in the lignin were removed, chlorolignin apparently containing two, and bromolignin containing only one, methoxyl group. Six of the twelve chlorine atoms in flax chlorolignin were eliminated with great ease, for example, by dissolving the fully chlorinated derivative in cold dilute sodium hydroxide, the hexachlorolignin being precipitated on acidification. Hexachlorolignin contains only one methoxyl group and therefore the fully chlorinated product, dodecachlorolignin, can contain only one such group, and is similar to the bromo-compound in that respect. The higher figure for methoxyl obtained on analysis is due to the ease with which hydrogen chloride is eliminated during estimation in the Zeisel apparatus. The Perkin method for the determination of acetyl also gives high results in the case of acetyldodecachlorolignin owing to the liberation of ethyl chloride.

The six wood lignins have been brominated and subsequently acetylated. The dodecabromolignins and their acetyl derivatives on analysis gave results agreeing closely with those obtained from the corresponding products derived from flax lignin (Table II). The dodecachlorolignins prepared from two wood lignins were similar in composition to flax dodecachlorolignin. A mixture of

the six wood dodecachlorolignins, on solution in dilute sodium hydroxide solution and reprecipitation with hydrochloric acid, gave a product comparable in all respects with flax hexachlorolignin. It may also be noted that the various acetylated dodecachlorolignins were more readily hydrolysed than the corresponding bromo-compounds, a behaviour similar to that of the derivatives from flax lignin, and that in all cases both acetyl derivatives were insoluble in cold sodium hydroxide solution.

A third type of derivative, nitrolignin, has been prepared from each wood lignin, and the products were identical with that from flax lignin in composition, three nitro-groups having been introduced into the molecule. As in the case of flax nitrolignin, a part of the nitrogen is present as organic nitrate, as is evident by the fact that a proportion can be estimated by the Lunge or Schultze-Tremann method. The total nitrogen, however, can only be determined by the Dumas or Kjeldahl method. The nitration of lignin proceeds equally readily whether nitric acid alone (40%) or a mixture of nitric and sulphuric acids is used, the products containing the same percentage of nitrogen. These facts indicate the probability of the presence of aromatic nuclei in lignin. Acetylnitrolignin is soluble in cold alkalis, and it is possible that nitrolignin contains one or more carboxyl groups. In this connexion it may be noted that elementary analysis of the nitro-compounds shows that some oxidation has taken place in addition to nitration. Owing to the ready hydrolysis of the acetylnitrolignins, it is difficult to deduce the number of hydroxyl groups in the molecule from analyses of this compound.

TABLE II.

Substance analysed.	Determination.	Source of Lignin. Flax.	Larch.	Pine.	Spruce.	Ash.	Birch.	Poplar.
Dodecabromolignin	C	28·0	28·2	—	—	28·1	—	—
	H	1·5	1·6	—	—	1·6	—	—
	Br	55·2	55·0	54·8	55·2	55·1	54·7	54·9
Acetyldodecabromolignin	OMe	1·8	1·6	—	—	—	2·4	2·1
	$CO{\cdot}CH_3$	9·4	9·8	9·0	9·8	—	—	9·2
Dodecachlorolignin	Cl	35·1	35·5	—	—	—	36·0	—
	OMe	5·2	4·9	—	—	—	5·1	—
Nitrolignin	C	50·4	50·2	—	50·6			
	H	3·8	3·8	—	3·9			
	N	4·2	4·1	4·1	—	4·3	—	4·2
	OMe	3·0	3·2	2·6	3·1	3·0	3·3	—
Hexachlorolignin	C	50·1			49·5*			
	H	3·0			3·2*			
	OMe	3·45			3·5*			
	Cl	20·8			20·4*			
Methyl-lignin-phenylhydrazone	N	—			7·5*			

* Samples prepared from a mixture of equal quantities of the wood lignins.

Some discussion has recently taken place in the literature as to whether or not lignin evolves furfuraldehyde on distillation with 12% hydrochloric acid, and in view of this we have carefully examined our products, using the volumetric method for the estimation of pentosans in wood cellulose previously described by us (*J. Soc. Chem. Ind.*, 1924, **43**, 35T). Average results for the six crude lignins obtained by acidification of the alkaline liquor showed the presence of 0·9% of pentosans. This value was reduced to 0·3% by one purification from acetone and hydrochloric acid, whilst the product from a second purification gave no trace of furfuraldehyde. We therefore regard as untenable the view of Hägglund (*Cellulosechemie*, 1923, **4**, 73) that lignin contains 5% of furfural-yielding carbohydrate as an integral part of the molecule.

Of the sixteen oxygen atoms present in the molecule of lignin, nine are in the form of hydroxyl groups and one as an aldehyde group. The presence of the latter was indicated by measurements of the amount of Fehling's solution reduced by lignin, and was confirmed in the case of flax lignin, by a volumetric determination of the amount of phenylhydrazine required to form the phenylhydrazone. The following experiment shows, however, that the monohydrazone is only formed under the mild conditions used in the volumetric method, and that the reaction can be made to proceed further. Methyl-lignin was allowed to react with a hot alcoholic solution of phenylhydrazine, and the product freed from phenylhydrazine by several precipitations from acetone and hydrochloric acid. Analysis showed that three phenylhydrazine molecules had reacted with each molecule of lignin, and therefore that two ketonic groups must also be present. Methyl-lignin was used instead of lignin in order to avoid the formation of a phenylhydrazine ester. These results may be summarised by writing the formula for lignol in the extended form

$$C_{38}H_{30}O_4(CO)_2(CHO)(OH)_9.$$

The details of the experimental work are similar to those given in Part I for flax lignin, and are therefore not repeated.

The results are published by permission of the Director of Artillery, to whom our thanks are due.

RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH. [*Received, October 21st*, 1924.]

XXIII.—*A Redetermination of the Atomic Weight of Bromine. The Inseparability of the Isotopes by Fractional Crystallisation.*

By Percy Lucock Robinson and Henry Vincent Aird Briscoe.

The only precise experimental evidence in support of the generally accepted view that isotopes are inseparable by fractional crystallisation is the attempt by Richards and Hall (*J. Amer. Chem. Soc.*, 1917, **39**, 531) to separate thus the isotopic forms present in lead derived from Australian carnotite. Both they and Soddy (J., 1911, **99**, 72; *J. Amer. Chem. Soc.*, 1917, **39**, 1614) refer to the earlier data, which need not be quoted here.

Richards and Hall obtained no evidence of separation by 904 effective crystallisations, but their lead presented a relatively unfavourable case, since it contained only about 20% of the heavier isotope and the nitrates of the isotopes differed in solubility by but 0·74% (Richards and Schumb, *J. Amer. Chem. Soc.*, 1918, **40**, 1403). Since Aston's work has disclosed the existence of isotopes of many of the lighter elements, it has become clear that cases may be found permitting a more precise test (or proof) of inseparability by fractional crystallisation. The isotopes of boron differ by 10% in atomic weight, but the isotope ratio is unfavourable (approximately 20% B^{10} and 80% B^{11}), and an accurate determination of the atomic weight is both difficult and laborious. A prolonged fractionation of boric acid was effected, but the determinations of atomic weight, although they had other unexpected features of interest (see following paper), proved valueless for the purpose now under discussion.

Bromine, in the form of ammonium bromide, seems to present the best test-case, because (1) bromine has but two isotopes (Br^{79} and Br^{81}), present in nearly equal proportions and differing by 2·2% in atomic weight, (2) hydrogen and nitrogen are "simple" elements and together form less than 20% of the salt, (3) the atomic weight of bromine can be determined by direct and trustworthy methods, and (4) ammonium bromide crystallises from water in a fashion convenient for a long series of fractionations.

Therefore, with the double object of making a re-determination of the atomic weight of bromine and of confirming, in this more favourable case, the finding of Richards and Hall, ammonium bromide was subjected to prolonged fractional crystallisation and the atomic weight of the bromine in the final head and tail fractions was determined by measurement of the ratio Ag : AgBr.

Purification of Reagents.

Water.—Laboratory distilled water, already free from halogen, was redistilled from a little caustic soda and potassium permanganate in a 10-gallon copper still through a vertical spray-trap packed with glass beads and condensed in pure tin. The first and last portions of the distillate were rejected and the main fraction was collected and stored (for but a short time) in 20-litre stoppered resistance glass bottles which had been well cleaned, steamed out and kept for months full of distilled water. Many nephelometric tests were made, but on no occasion did the water give any indication of chloride.

Ammonia.—Ammonia gas, liberated by warming the purest commercial ammonia ($d = 0{\cdot}880$), was dissolved in pure water, in an apparatus constructed entirely of resistance glass with a ground-in leading tube.

Sulphur Dioxide.—The gas, used both for the conversion of bromine to hydrobromic acid and for the precipitation of silver by Stas's method, was always obtained from the middle fraction of a syphon of the liquid.

Nitric Acid.—Commercial nitric acid, containing only small traces of halogen, was thrice redistilled in an apparatus constructed of " Duro " resistance glass with ground joints, large head and tail fractions being rejected. The final main fraction, tested in the nephelometer, was free from halogens. It was kept in a resistance glass bottle having a well-ground glass stopper protected by a glass cap.

Formic Acid.—The purest obtainable reagent acid was twice redistilled from a fused silica flask having a ground-in silica condenser and adapter. Considerable head and tail fractions were rejected in each distillation, and the main fraction was preserved in a stoppered silica flask.

Magnesia.—Magnesium nitrate was thrice precipitated from saturated aqueous solution by excess of nitric acid, filtered on porcelain, dissolved in water, and precipitated with ammonia. The hydroxide was washed by decantation, filtered, dried at 100°, ignited in air in a platinum dish, and finally heated at about 1000° in a current of moist pure hydrogen. Magnesia boats, moulded from the pure oxide moistened with dilute nitric acid, were ignited and used on a silica plate.

Hydrochloric Acid.—Commercial reagent acid was freed from arsenic by treatment with a copper-tin couple and distillation from copper gauze according to the method of Thorne and Jeffers (*Analyst*, 1906, **31**, 101).

Zinc.—A sample of granulated electrolytic zinc, kindly supplied

by Messrs. Brunner Mond & Co., Ltd., proved to be free from arsenic and was used without further purification.

Hydrogen.—This gas, prepared from pure hydrochloric acid, containing a little platinic chloride, and pure zinc in a Kipp's apparatus, passed to a purifying train, the several parts of which were sealed together, in which it traversed successively a 12 inch column of concentrated potassium hydroxide solution, two 12 inch columns packed with broken sticks of potassium hydroxide, and two 10 inch columns packed with phosphorus pentoxide distributed on glass wool.

Silver.—Two samples, "A" and "B," were used, prepared in the same way but at different times and from different samples of commercial silver nitrate. In each case a filtered aqueous solution of silver nitrate (200 g.) was precipitated in a volume of about 20 litres with ammonium bisulphite according to the method of Stas (Briscoe, J., 1915, **107**, 69). The precipitated silver was washed six times with dilute ammonia, allowed to stand over-night with ammonia, washed six times with water, and dried at 100°. This silver, in 100 g. portions, was dissolved in pure nitric acid, precipitated hot with ammonium formate in a bulk of 2 litres, well washed with ammonia and water, and dried, first at 100° and finally at 250°, in an electrically heated covered beaker.

Before weighing, the silver was melted on a boat of pure magnesia in an atmosphere of hydrogen in an electrically heated silica tube furnace. The hydrogen issuing from the furnace during melting contained no impurities detectable by Marsh's test or by smell. At the end of each fusion the silver was collected into large buttons by shaking the furnace and these, when cool, were etched with 1 : 1 nitric acid, well washed with water, heated at 250° for 12 hours, and cooled in a desiccator over solid potassium hydroxide.

The Determination of Weight.

All precise weighings were made on an Oertling balance constructed specially for this work, resembling in many respects the standard type known as "No. 7, S.W.," but with a beam of Firth's 36% nickel-steel having a low coefficient of expansion, pan-supports of special design, and a separate enclosure for the beam after the principle used by Manley (*Phil. Trans.*, 1910, **210**, *A*, 387). No proper situation giving constant temperature and freedom from vibration was available for the balance: it was used on an ordinary stout wooden table in a room subject to vibration and to considerable and rapid fluctuations of temperature. Even under these adverse conditions, it gave results sufficiently precise and consistent for this work, a remarkable performance which is undoubtedly

attributable to the special features of construction indicated above.

The sensitiveness of the balance increased very slightly with the load and during all the work here described was very nearly 100 scale divisions per milligram. In weighing by the method of oscillations, the zero could easily be determined to the nearest half-division and the apparent weight thus ascertained with an error not exceeding 0·00001 g. A set of gold-plated brass weights with platinum fractions by Oertling and a gold 5-mg. rider were used and were calibrated to ascertain the relative weights in air on three separate occasions before and during the weighings. The corrections applied to ascertain relative weights in a vacuum were calculated using the density of air at the temperature and pressure observed during the weighing and the densities 10·49 and 6·47 for silver and silver bromide, respectively. As relative weights only were desired and the inequality of the arms of the balance was very small and constant, all weighings were made directly. All were made in duplicate and many in triplicate: in no case did the values for the vacuum weight thus obtained differ by more than 0·00003 g., thus it seems probable that the mean values are in error by less than this amount.

Silver was weighed directly on the balance pan: silver bromide was weighed in a stoppered glass bottle against a tare of the same glass and of closely similar form, volume and weight which had been treated in all respects as the bottle.

The balance case contained solid caustic potash and a piece of pitchblende.

The Fractional Crystallisation of Ammonium Bromide.

As starting material, commercial ammonium bromide, puriss., was used. Prolonged exposure to the laboratory atmosphere and contact with glass inevitably introduce impurities compared with which those originally present are insignificant; hence no attempt was made to ascertain the nature and amount of the latter.

About 2500 g. of ammonium bromide were dissolved in hot water in such proportion that about one-half crystallised out on cooling. Each fraction was again fractionated in a similar manner until a series of 30 fractions had been built up. Thereafter the number of fractions was kept constant and fractionation was continued in the usual way, by crystallising the whole series, taking away the "head" (most soluble) mother-liquor to form part of a new fraction, transferring each of the other mother-liquors to the crystals of the next higher fraction, adding water to the crystals of the "tail" (least soluble) fraction, and again crystallising the whole series.

A detailed scheme of such a fractionation is given by Richards and Hall (*loc. cit.*). In all, 80 crystallisations of the whole series were thus made * and the total number of crystallisations, including those involved in the establishment of the series, was approximately 2700.

Throughout the later part of the fractionation each fraction contained about 80 g. of ammonium bromide, of which one-half was transferred at each crystallisation. The fractions were contained in 200 c.c. conical flasks closed against dust by loose hollow glass stoppers: distilled water of good quality was used for all crystallisations.

At the end of the fractionation, the extreme end fractions, Nos. 42 and 72, were rejected and the ammonium bromide of Nos. 43, 57 and 71, the "tail," middle, and "head" fractions, respectively, was taken for the atomic weight determinations.

Purification of Bromine for Analysis.

The volatility of bromine and its liberation from a bromide by oxidation afford an unexceptionable means of separating it sharply from all elements other than chlorine and iodine. It is therefore with these elements, which would tend to concentrate in the tail and head fractions respectively, that the scheme of purification is concerned. At the same time, as it was important that the determinations on head and tail fractions should be strictly comparable, both had to receive identical treatment.

Bromine is usually purified from the other halogens by applying the facts that it liberates iodine from an iodide, and is itself liberated from a bromide by chlorine. Whilst in ordinary analytical work the assumption that these reactions are complete and irreversible holds well enough, they are probably not so in fact (see, *e.g.*, Schuyten, *Chem. Ztg.*, 1908, **32**, 619). The methods usually adopted for the rigorous purification of bromine for atomic weight work (see, *e.g.*, Scott, J., 1900, **97**, 614; Baxter, *J. Amer. Chem. Soc.*, 1906, **28**, 1322) reject so great a proportion of the material in head and tail fractions (using "head" and "tail" here in a chemical sense) as to ensure elimination of the other halogens, but were for that reason inapplicable to the small quantities (50—60 g. of bromine in each fraction) available for purification in this case.

Therefore each fraction of ammonium bromide was evaporated to dryness, dried at 160°, and weighed. A quantity of pure sodium carbonate, about 5% in excess of the calculated amount, dissolved in a small quantity of water, was added to the bromide and the

* The establishment of the series and the first 30 crystallisations thereof were carried out by Mr. T. Hanby, whose valuable assistance in this tedious work we desire to acknowledge.

whole was again evaporated to dryness and fused at about 800° in platinum in an oxidising atmosphere. Thus any organic impurities were destroyed.

A solution of about 1 g. of potassium dichromate and 30 c.c. of concentrated sulphuric acid in 170 c.c. of water was boiled vigorously for 10 minutes to expel any possible trace of halogen, cooled, and used to dissolve the sodium bromide from the platinum dish. This solution was transferred to the flask A of the distillation apparatus shown in Fig. 1, heated and kept boiling for about 10 minutes whilst the column B, jacketed with cold water, acted as a reflux condenser so that the free bromine might react with any trace of iodide present. Then the cooling was discontinued and the solution boiled until the bromine had distilled over into a flask containing pure water cooled externally by ice. Finally this flask was removed so that steam passed uncondensed right through the apparatus and carried away any residual traces of free halogen. The quantity of potassium dichromate used was calculated to displace about 2% of the total bromine, and the procedure described evidently favoured the elimination therewith of any trace of iodine.

After cooling, the flask was detached from the apparatus and into it was introduced a further quantity of potassium dichromate (35—45 g.) calculated to displace about 95% of the total bromine originally present. Then A was refitted to the condenser, heated very slowly, at first using B as a reflux condenser and later distilling slowly over into a flask as already described. Thus a main fraction of bromine and bromine water was obtained under conditions favourable to the reaction of any trace of chlorine with the residual bromide in solution. As a check, this solution was in each case treated with an excess of potassium dichromate and distilled a third time : the liberation of 1—2 g. of bromine afforded satisfactory evidence that excess of bromide had been present during the distillation of the main fraction.

Tests made with the largest (middle) fraction showed that digestion with sodium oxalate was unsatisfactory as a means of conversion to sodium bromide, and that the quantities available were too small to permit a satisfactory distillation of aqueous hydrobromic acid. Therefore, in working up the end fractions of ammonium bromide, the main fraction of bromine from the first oxidation was converted directly to hydrobromic acid by the use of sulphur dioxide, and the acid was subjected to a second fractional oxidation with potassium dichromate as already described.

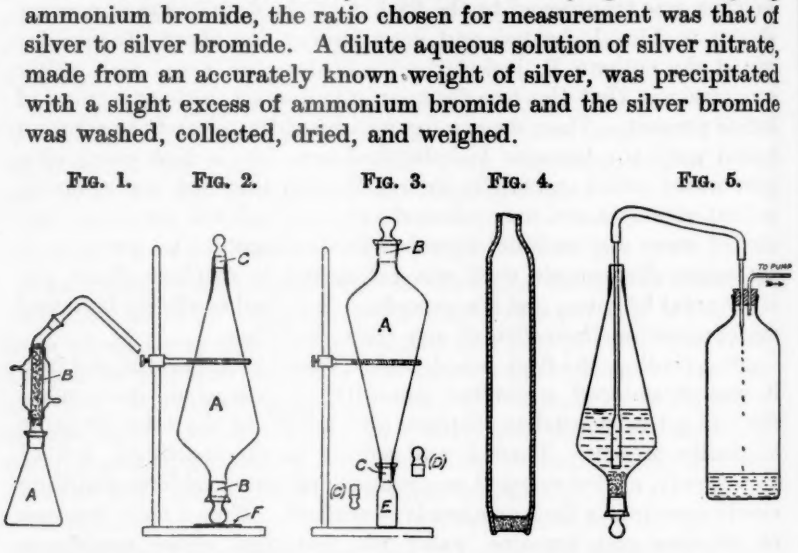
Thus it was possible to obtain in each final main fraction of the second series of oxidations about 90% of the bromine present in the original ammonium bromide. This bromine was collected in an

excess of pure dilute aqueous ammonia and the resulting ammoniacal solution of ammonium bromide was transferred to a carefully cleaned, stoppered, resistance glass bottle which was kept free from dust in a clean desiccator until required for analysis.

Method of Analysis.

To avoid the uncertainty attendant on drying and weighing ammonium bromide, the ratio chosen for measurement was that of silver to silver bromide. A dilute aqueous solution of silver nitrate, made from an accurately known weight of silver, was precipitated with a slight excess of ammonium bromide and the silver bromide was washed, collected, dried, and weighed.

FIG. 1. FIG. 2. FIG. 3. FIG. 4. FIG. 5.



Platinum Gooch-Munroe crucibles were not available, so another method of collecting the precipitate was sought, and, as any transference is attended by risk of loss and is a source of doubt and anxiety, it seemed desirable, if possible, to collect and weigh the precipitate in the vessel in which it is formed but at the same time to avoid any weighing of large glass vessels. After several attempts, a satisfactory method was evolved whereby the precipitate was collected in a detachable part of a suitably shaped precipitation flask shown in Figs. 2 and 3.

A conical flask, A, of about 1700 c.c. capacity has two necks, B and C, fitted with hollow glass stoppers; the neck C has also an external taper, both this and the stopper D being ground into the neck of the weighing bottle, E. Four such flasks and two spare weighing bottles with stoppers, for use as tares, were made of "Durosil" glass, the joints and stoppers being very carefully ground and polished to an excellent fit: * the various parts of each set

* Our thanks are due to Mr. G. Ellison of this Department for his care and skill in executing this difficult task.

were etched with the same number. Before use the flasks and bottles were cleaned with chromic and nitric acids, washed, allowed to stand about three weeks containing a solution of ammonium bromide and nitric acid, allowed to soak for a further period in distilled water, and well washed.

In conducting a precipitation several buttons of pure silver, weighing about 4—5 g., were weighed, and dissolved in pure nitric acid in a solution flask of the form previously described (Briscoe, J., 1915, **107**, 78), and the solution was boiled to expel nitrous fumes, cooled, and diluted with pure water to about 400 c.c. Meanwhile a measured volume of ammonium bromide solution, containing bromine about 5% in excess of that required by this silver, was acidified with pure nitric acid, diluted to about 700 c.c., and filtered into the precipitation flask supported by a padded ring and resting on a pad of filter paper, F, in the position shown in Fig. 2.

All succeeding operations up to and including the final weighings were conducted in orange light in a darkened laboratory set aside for this work. A rapid rotary movement was given to the bromide solution, the silver solution was poured into it with all the usual precautions to avoid loss, and 6—8 rinsings of the solution flask followed, bringing the total bulk in the precipitation flask to about 1400 c.c. Then the flask was stoppered and vigorously shaken, at first every 30 mins. and later about twice a day. After 7 days, the precipitate having become sufficiently dense and coherent for transference, the stopper C was removed and rinsed into the flask, and the supernatant liquor was syphoned off by means of the arrangement described later. By careful manipulation, the liquor left above the precipitate was reduced to 2—3 c.c.

Next the silver bromide was washed twice by decantation, using in each case about 1000 c.c. of wash-water, allowing the precipitate to settle 2—3 days, and syphoning off as in the first case. Commonly the precipitate tended to form a colloidal solution in the second wash, and a solution of about 0·5 g. of ammonium nitrate, prepared from pure ammonia and nitric acid, was added to avoid this difficulty.

Transference of the precipitate to the weighing bottle was effected by means of the second washing. The bottle, having been carefully heated in dry air, cooled, and weighed against the tare, was fitted to the flask at C and by reversing the whole apparatus into the position shown in Fig. 3 and alternately giving a rotary agitation and allowing the apparatus to stand, the silver bromide was washed down into E. Then the stopper B was removed, the wash-water syphoned off, the syphon tube and the walls of the flask were rinsed down with a fine jet of water, and the wash was syphoned off.

Finally the syphon was partly withdrawn, it and the flask were again rinsed, the bottle was detached, and the neck C rinsed into it.

The bottle containing the silver bromide with but 15—20 c.c. of water was then heated in an electrically heated sheet nickel air-bath, first at 85—90° until all free water had evaporated and then at about 250—300° for 12—14 hours. During the whole of this drying operation a current of air, supplied by a water-blast and dried by passing through a glass train over sulphuric acid, concentrated aqueous potassium hydroxide, and solid potassium hydroxide successively, was led into the bottle by a glass tube inserted through the lid of the oven. The tare was, of course, heated alongside the bottle and after cooling, usually for 3—4 hours in the current of dry air, both bottle and tare were stoppered, transferred to the balance case, and weighed. The heating and weighing were repeated once or twice to ensure that a constant weight had been attained.

In two of the preliminary experiments the silver bromide was afterwards fused in the bottle, heated in a small vertical electric furnace of silica provided with a window to allow observation of the fusion. As this treatment had no appreciable effect upon the apparent weight, it was omitted in the final analyses.

To minimise the risk of appreciable solvent action on the bottles, care was taken that they were never in contact with washings for more than 12 hours. There remains the risk of mechanical loss of glass from the ground joint; although Richards has shown that with a well made and carefully used joint this risk is small. Fortunately, satisfactory evidence that both these effects were negligible in the present work is afforded by comparing the weights of three of the bottles (weighed against the same tare) before and after the first series of precipitations :—

	Bottle I.	Bottle II.	Bottle III.
Apparent wt. before	2·02985	2·22330	3·22103
„ „ after	2·02987	2·22330	3·22104

Before the method above described was finally adopted, attempts were made to find a substitute for the Gooch-Munroe crucible which may be recorded briefly here. An alundum crucible was digested with 1 : 2 nitric acid for 6 hours and with repeated changes of water for 24 hours, washed thoroughly with water under suction, dried at 130° for 10 hours, and ignited to about 600° in a closed porcelain crucible. After cooling in a desiccator and standing on the balance pan for 30 minutes, the crucible had a weight of 12·47830 g. Then a litre of a clear filtered solution of 20 g. of ammonium bromide in 10% nitric acid was passed through the crucible, and it was washed and dried as before, when its weight was 12·47799 g. (loss 0·30 mg.). A repetition of the treatment reduced the weight to

12·47782 g. (loss 0·17 mg.) and a second repetition, using 5% nitric acid, caused a further change to 12·47746 g. (loss 0·36 mg.). Thus, evidently there was a continuous and variable loss too great to permit the successful use of alundum crucibles. A Jena filter crucible having a mat of sintered glass, similarly treated but dried for 14 hours at 350°, lost in weight 0·80 mg.: and among several such crucibles it was observed that the degree of fritting was not uniform, some mats being so friable that glass could be removed with the finger nail. Hence such crucibles, too, were dismissed as unsuitable.

The device used in syphoning the liquors and washings may here be described. Preliminary experiments showed that as the liquid level fell, fine particles of precipitate were apt to be dislodged from the sides of the flask and carried over with the washings. It was impracticable to reduce the syphon to a capillary fine enough to stop these particles, therefore, although the syphon was never brought in contact with the mass of the precipitate, some form of reverse filter was necessary. Disks of thin alundum or wads of spongy platinum fused into the ends of glass tubes proved much too slow, but a porous glass filter of the form shown in Fig. 4 proved satisfactory. It was made by taking powdered Durosil glass passing a sieve of 100 meshes to the linear inch and retained on a 200 mesh sieve, cleaning the powder by boiling with hydrochloric acid and washing with water, packing it wet to form a 3 mm. layer in the end of a 12 mm. bore Durosil tube, and then drying at 100° and heating carefully in a luminous flame until the glass sintered to a strong, coherent yet porous mass adhering firmly to the tube. After experience had been gained, it was possible thus to make filters which would pass 1000—1500 c.c. of water per hour with a pressure difference of 30—40 cm. of mercury and yet retain the finest particles of suspended matter.

Each filter was fused to a long tube and then carefully cleaned and soaked. In use it was connected by a length of clean pure rubber pressure-tubing to a clean bottle in which the liquors were received in the manner shown in Fig. 5.

In each analysis the first mother-liquor was tested to ensure that an excess of bromide had been used: as nephelometric tests gave in them no indication of silver, they were rejected. Some small particles of silver bromide adhered to the inner surface of the precipitation flask or were retained by the glass filter: therefore one filter was kept for each analysis and after the bottle and precipitate had been removed, the flask was stoppered at B and re-inverted, and a small quantity of pure ammonia was passed in the reverse direction through the filter, shaken round the walls of the flask and, with the rinsings of filter and flask, made up to a definite bulk.

The silver content of this solution and of the main washings was then determined by nephelometric comparison of aliquot portions with standard silver solutions, and the weight of silver lost thus ascertained was deducted from the weight of silver originally taken.

Statement and Discussion of Results.

Several preliminary analyses, made on the middle fraction of ammonium bromide, No. 57, whilst useful in establishing the methods, are not comparable in value with those of the final series: hence the results are omitted here.

The final series consisted of eight determinations, four on the ammonium bromide from the head fraction No. 71 and four on that from the tail fraction No. 43. The essential data are given in Table I.

TABLE I.

Number of analysis.	Fraction of bromine.	Sample of silver.	Vacuum wt. (g.) of silver taken.	Silver (g.) lost in washings, etc.	Corrected vacuum wt. of silver.	Vacuum wt. (g.) of silver bromide.	Ratio Ag/AgBr.	Atomic weight of bromine.	Difference from mean.
Series I.									
1	71	A	3·69325	0·00058	3·69267	6·42874	0·574400	79·933	+0·019
2	„	„	5·06115	0·00297	5·05818	8·80494	0·574471	79·910	−0·004
3	„	„	3·93515	0·00374	3·93141	6·84337	0·574484	79·906	−0·008
4	„	„	3·67332	0·00097	3·67235	6·39249	0·574479	79·908	−0·006
				Mean of Series I.			0·574459	79·914	±0·009
Series II.									
5	43	A	5·14730	0·00146	5·14584	8·95708	0·574499	79·901	−0·015
6	„	„	3·08140	0·00111	3·08029	5·36261	0·574401	79·933	+0·017
7	„	B	3·34631	0·00072	3·34559	5·82369	0·574479	79·907	−0·009
8	„	„	3·43817	0·00251	3·43566	5·98102	0·574427	79·916	+0·002
				Mean of Series II.			0·574451	79·914	±0·011
				General mean			0·574455	79·914	±0·010

In the first group of analyses the extreme variation in the ratio Ag : AgBr is 0·000084 or 1 part in 6840 : that in the atomic weight of bromine is 0·027 or 1 part in 2960. In the second group the corresponding variations are 0·000096 or 1 part in 5984 and 0·032 or 1 part in 2493. The magnitude and sign of these variations indicate that the mean value of the atomic weight deduced from each series has an error probably less than 0·01 or, in round numbers, about 1 part in 8000. The mean atomic weights from the two series differ by but 1 part in 40,000 : as a change of 1% in the isotope ratio would change the atomic weight by 0·02 and should have been appreciable in these determinations, it appears that a fractionation of ammonium bromide involving 2700 crystallisations does not produce such a change.

This result, affording as it does more precise confirmation of the

conclusion drawn by Richards and Hall, is of some theoretical interest. It is, in particular, instructive to institute a comparison between the present results and those recorded for salts of kindred rare-earths, where the solubility differences are of the same order.

The solubilities of the hexahydrated nitrates of lanthanum and neodymium, $La(NO_3)_3,6H_2O$ and $Nd(NO_3)_3,6H_2O$, are respectively, 151·1 and 152·9 parts of anhydrous nitrate in 100 parts of water (James and Whittemore, *J. Amer. Chem. Soc.*, 1912, **34**, 1168; James and Robinson, *ibid.*, 1913, **35**, 754). As the molecular weights are 324·8 (La = 138·8) and 330·2 (Nd = 144·2), the *molecular solubilities* are 0·46520 and 0·46515. The coincidence of these numbers within one part in 9000 is obviously accidental, but the molecular solubilities evidently differ by no more than the error of the solubility determinations, say 2 or 3 parts in 1000 parts.

The effect of fractional crystallisation in this case is shown in the investigations, *inter alios*, of Demarçay (*Compt. rend.*, 1896, **122**, 728; 1900, **130**, 1021) and of Baxter and Chapin (*J. Amer. Chem. Soc.*, 1911, **33**, 1). In the latter case, for example, about 1600 crystallisations as double ammonium nitrates and about 1300 as simple nitrates produced a number of fractions of neodymium free from appreciable traces of other earths.

The fact that 2000 crystallisations or fewer completely separate these earths whilst more than 2500 crystallisations do not appreciably change the proportions of the two kinds of molecule in ammonium bromide may be explained by, and therefore affords chemical evidence supporting, the theories of Bohr and of Bury (*J. Amer. Chem. Soc.*, 1921, **43**, 1602) whereby the additional electrons in the atom of the heavier of a pair of rare-earth metals are supposed to be less intimately associated with the corresponding protons than are the additional electrons in the heavier of a pair of isotopes.

Regarding the data as one series of determinations of the atomic weight of bromine, it is to be noted that the extreme variation in the ratio Ag : AgBr is from 0·574400 to 0·574498 or 1 part in 5745, whilst that in the atomic weight is from 79·901 to 79·933 or 1 part in 2500. The general mean values are given in Table I.

A discussion of all the available data for the ratio of silver to silver bromide, both direct and indirect, has been given by Clarke ("A Recalculation of the Atomic Weights," 4th Edition, *Mem. Nat. Acad. Sci.*, 1920, **16**, 71) and need not be attempted here. The best direct determinations are those of Baxter (*J. Amer. Chem. Soc.*, 1906, **28**, 1322), whose general mean of 18 determinations of the ratio Ag : AgBr is 0·57445, a figure substantially identical with that calculated by Clarke as the general mean of all determinations.

Possible sources of error in the present determinations are :

(1) errors in weighing; (2) loss of silver in transference; (3) impurity in the silver; (4) loss of silver bromide mechanically or in solution; (5) the presence of chlorine or iodine in the ammonium bromide. The error in weighing was undoubtedly too small to have any significant effect and the mode of transference of silver solution to the precipitation flask would appear to eliminate any risk of mechanical loss. The methods used for the preparation of pure silver have been shown to yield a metal containing less than 1 part of impurity in 300,000 parts of silver (Briscoe and Little, J., 1914, **105**, 1320). There can be little doubt that the chief error in the determination of weight lay in the nephelometric estimation of the silver lost (4) in washings and retained by the flask and filter: a careful review of the analytical details leads to the conclusion that this error was not greater than 0·0001 g., but it was probably the one really significant error in the determinations. With regard to the purity of the bromine, it is certain that in such a prolonged fractionation the whole of any chlorine and iodine originally present would have become concentrated in opposite end fractions: therefore the identity of the results obtained with these fractions shows that the chemical purification subsequent to fractionation had so far reduced the proportion of these halogens that their effect on the atomic weight of bromine was inappreciable.

The final mean value of the ratio Ag : AgBr now found differs from Baxter's value by less than 1 part in 100,000, and the rounded mean value of the atomic weight Br = 79·92, with a probable error ± 0·0031, confirms the accepted atomic weight.

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NEWCASTLE UPON TYNE. [*Received, November 3rd*, 1924.]

XXIV.—*The Use of Fused Borax in the Determination of the Atomic Weight of Boron.*

By HENRY VINCENT AIRD BRISCOE, PERCY LUCOCK ROBINSON, and GEORGE EDWARD STEPHENSON.

THOUGH a few determinations of the atomic weight of boron have been made by ascertaining the ratio of boron halides to silver, the majority have depended in one way or another upon weighing anhydrous borax in the form of borax-glass. A detailed discussion of the results may be found in Clarke's "A Recalculation of the Atomic Weights" (*Mem. Nat. Acad. Sci.*, 1920, **16**, 205) and it is sufficient here to give a list of the determinations. Table I records all the previous data, classified according to the nature of the method employed: the wide divergence among the results renders

the "probable errors" obviously valueless as a measure of the weight to be given to each determination, and they are, therefore, omitted.

TABLE I.

Previous Determinations of the Atomic Weight of Boron.

A. Determinations dependent upon weighing fused borax:

1826. 1849.	*Berzelius* } *Laurent* }	*Estimation of water in borax.*	*11·023*
1869.	*Dobrovolsky.*	*Estimation of water in borax. 1st series.*	*10·859*
		2nd series.	*11·529*
1892.	*Hoskyns-Abrahall.*	*Decahydrate to borax glass.*	*10·703*
1893.	Ramsay and Aston.	Decahydrate to borax glass.	10·946
		Borax glass to sodium chloride.	10·955
		Borax glass to silver chloride.	11·059
1898.	Armitage.	Decahydrate to borax glass.	10·986
		Borax glass titrated with sulphuric acid.	10·933
1918.	Smith and van Haagen.	Borax glass to sodium sulphate.	10·904
		Borax glass to sodium fluoride.	10·903
		Borax glass to sodium carbonate.	10·905
		Borax glass to sodium nitrate.	10·899
		Borax glass to sodium chloride.	10·901
		Mean of all determinations.	10·964
		Mean excluding the first four results.	10·939

B. Determinations of the ratio of a boron halide to silver or silver halide:

1892.	Hoskyns-Abrahall.	$BBr_3 : 3Ag$.	10·800
1899.	*Gautier.*	*$BBr_3 : 3AgBr$.*	*11·016*
		$BCl_3 : 3AgCl$.	*10·947*
1922.	Hönigschmid and Birkenbach.	BCl_3 : 3AgCl.	10·840
			10·818
			10·825
		Mean excluding Gautier's results.	10·827

C. Determinations of ratios which do not involve fused borax or a boron halide:

1893.	Rimbach.	$Na_2B_4O_7 10H_2O$: hydrochloric acid solution.	11·006
1899.	*Gautier.*	*$B_2S_3 : 3BaSO_4$.*	*11·024*
		$B_4C : 6CO_2$.	*10·997*
1923.	Stock and Kuss.	$B_2H_6 : 6H_2$.	10·806

References: Berzelius, *Pogg. Ann.*, 1826, **8**, 1; Laurent, *J. pr. Chem.*, 1849, **47**, 415; Dobrovolsky, *Doctoral Dissertation, Kiev*, 1869; Hoskyns-Abrahall, J., 1892, **61**, 650; Ramsay and Aston, J., 1893, **63**, 211; Armitage, P., 1898, **14**, 22; Smith and van Haagen, *Carnegie Inst. Washington*, Publication No. **267**, 1918; Gautier, *Ann. Chim. Phys.*, 1899, [vii], **18**, 352; Hönigschmid and Birkenbach, *Ber.*, 1923, **56**, [*B*], 1467; Rimbach, *Ber.*, 1893, **26**, 164; Stock and Kuss, *Ber.*, 1923, **56**, [*B*], 314; *Z. anorg. Chem.*, 1923, **128**, 49.

Certain of these determinations (printed in italics) are unsatisfactory. In Group A, those of Berzelius and Laurent have no pretensions to great accuracy, Dobrovolsky's two series are so

gravely discordant as to be valueless; and Abrahall's results are definitely those of preliminary analyses: thus these may be excluded, making the mean result for the Group, B = 10·939. In Group B, Gautier's results show discordance so grave, and so unaccountable in a halide ratio, as to necessitate their immediate exclusion: the remaining results give the mean value B = 10·827. In Group C, Gautier's determinations involve eccentric ratios apparently unsuitable for atomic weight determination. The two remaining values may be retained, but are not pertinent to the point now to be discussed.

Reviewing all the results in Groups A and B not excluded for the reasons given, it is immediately obvious that those dependent upon fused borax have a general tendency to be higher by about 0·1 than those deduced from halide ratios. As experience has shown that the halide ratios usually afford a very trustworthy means of determining atomic weights, and as, moreover, determinations in this laboratory, which will form the subject of another communication, confirmed the general result thereby attained, we were led to suspect that in the use of borax there lay some hitherto unsuspected source of systematic error.

The present determinations were therefore undertaken with a two-fold object: first, to obtain independent confirmation of the values for the atomic weight of boron obtained by earlier workers by the analysis of borax; and secondly, to attempt to ascertain whether the fractional crystallisation of boric acid from aqueous solution produces any change in the isotope ratio of boron. As, for reasons which will appear in due course, the results give no information on the second point and as the general nature of such an enquiry has been discussed elsewhere (Robinson and Briscoe, preceding paper), this secondary object need but be mentioned here in explanation of the nature of the boric acid used as starting material.

Outline of the Method.

Of the possible means of analysing borax, its titration with aqueous hydrochloric acid was chosen because the experimental procedure is relatively simple and therefore little liable to error, and because borax can thus be referred directly to silver chloride, for which the antecedent atomic weights are well known. Rimbach (*loc. cit.*), in his work upon the titration of borax decahydrate, has shown that the reaction proceeds quantitatively according to the equation :

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3.$$

Preliminary tests described later showed that the end-point could

be observed with an accuracy sufficient for our purpose, and the work of Smith and van Haagen afforded the strongest evidence that fused borax was a definite compound well suited to precise work. Therefore the following method was adopted:

Borax, prepared from boric acid and pure sodium carbonate, was purified by fractional crystallisation with centrifugal drainage of the crystals, and the borax decahydrate obtained was fused in platinum vessels in an electrically heated muffle furnace in a current of dry air free from carbon dioxide. The resultant borax glass was weighed, dissolved in water, and titrated with $N/5$-hydrochloric acid solution delivered from a weight burette; the titration being completed by the addition of $N/100$-acid solution from an accurately calibrated burette, using methyl-red as indicator. The acid was standardised by taking a weighed quantity and precipitating the whole of the chlorine as silver chloride, which was collected, dried, and weighed. Hence the ratio actually determined was $Na_2B_4O_7 : 2AgCl$.

The Determination of Weight.

All weighings of borax and silver chloride were made on the special Oertling balance sensitive to 0·01 mg. or less, already described (Robinson and Briscoe, *loc. cit.*), with weights carefully calibrated for relative weight in air and all usual precautions. Fused borax was weighed directly on the balance pan: silver chloride was weighed in the tared bottle used to collect the precipitate.

The standard acid solution was weighed in a stoppered burette, using another similar burette as tare, on a standard No. 7 S.W. Oertling balance carrying a load of 300 g. in each pan and sensitive to 0·1 mg. A second set of calibrated weights was used in this case. As the standard solution only served as a means of referring borax to silver chloride, the relation of the second set of weights to the first is immaterial.

The relative vacuum weights of borax and silver are given to the nearest 0·01 mg., those of standard acid to the nearest 0·5 mg. The vacuum corrections applied were calculated using the densities: silver chloride, $D = 5{\cdot}50$; borax, $D = 2{\cdot}357$ (Smith and van Haagen, *loc. cit.*).

Preparation of Reagents.

The *water* and *nitric acid* were prepared by the methods described in a recent communication (Robinson and Briscoe, *loc. cit.*) and the *silver* used was a part of the stock prepared for the work there described.

Hydrochloric Acid.—About 3 litres of pure reagent acid, main-

tained at boiling point in a glass flask, were treated for 30 minutes with a rapid current of chlorine gas from a cylinder of liquid chlorine, and the excess of chlorine was then boiled off. Thus any traces of bromine and iodine were removed. The acid then stood over-night with copper foil, previously cleaned with nitric acid and distilled water, to remove arsenic.

FIG. 1.

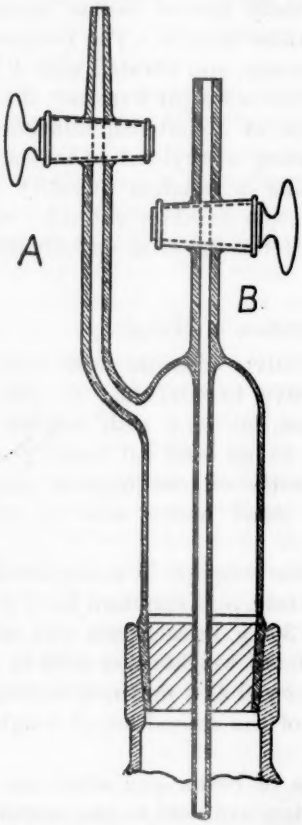
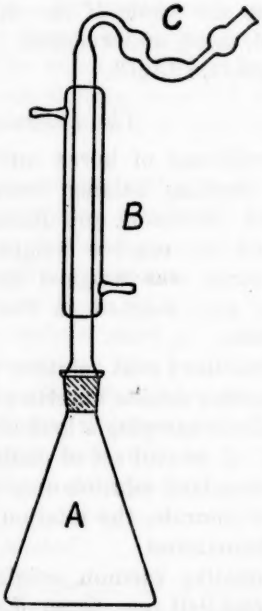


FIG. 2.



Next day the acid was transferred to a resistance glass still fitted with a ground-in condenser, heated for 15 minutes to cause a vigorous evolution of hydrogen chloride gas and thus to eliminate any remaining volatile impurity, and finally diluted to a density of 1·10 and twice distilled, considerable head and tail fractions being rejected in each distillation. The main fraction from the second distillation was used forthwith for the preparation of the standard acid. The approximate strength of the acid having been determined by diluting a weighed portion and titrating it against

fused borax, the requisite volume of the acid was transferred to the storage bottle and diluted to 4000 c.c. with pure water.

In order to ensure, as far as possible, that the concentration of the standard acid should remain constant during the series of titrations, the storage bottle was fitted with a well-ground glass stopper of the form shown in Fig. 1, where A is a stopcock and capillary tube for delivery of acid and B is a second tube, passing to the bottom of the bottle and also fitted with a stopcock to admit air when, the bottle being inverted, acid was withdrawn. Before each withdrawal of acid the contents of the bottle were mixed by vigorous shaking and, in order to minimise the volume of acid withheld from this agitation, the tube B was made of capillary bore. This stopper was wired in place and was not removed during the whole series of standardisations and analyses. Before use, the bottle had been well cleaned and rinsed, allowed to stand for some weeks full of approximately $N/5$-hydrochloric acid, and then again well washed with water.

A quantity of approximately $N/100$-acid was prepared by diluting in a calibrated flask a weighed quantity of the standard $N/5$-acid: thus it was possible by use of an appropriate factor to convert the volume of $N/100$-acid used in each titration to the corresponding *weight* of $N/5$-acid, which was added to the weight determined in the weight burette.

In the standardisation of the $N/5$-acid, a weighed quantity was delivered into a slight excess of aqueous silver nitrate, prepared from pure silver and nitric acid, and the precipitated silver chloride was collected, washed, and weighed by the method already described (Robinson and Briscoe, *loc. cit.*). In this case, of course, the chloride found nephelometrically in the washings and ammoniacal rinsings was calculated to silver chloride and added to the observed weight.

The essential data of the standardisations are given in Table II.

TABLE II.

	I.	II.
Vacuum weight of acid taken	154·4826 g.	160·9230 g.
Vacuum weight of silver chloride	4·52544 g.	4·71377 g.
Ratio, silver chloride : hydrochloric acid ...	0·0029294	0·0029292
Mean value of ratio	0·0029293	

All flasks and burettes used here and in the titrations were carefully calibrated by weighing out with water in the usual way.

Fractional Crystallisation of Boric Acid.

About 14 kilos of commercial boric acid supplied by Messrs. Borax Consolidated Ltd, but of unknown origin, were fractionally

crystallised (about 70 crystallisations) until two series, A and B, each of 19 fractions, were obtained. Each fraction contained about 350 g. of boric acid dissolved in 1500 c.c. of water. The fractions were contained in 2-litre round Jena flasks, fitted with loose glass stoppers to exclude dust: crystallisation was effected by slowly heating the whole set of flasks to boiling on a large hot plate and allowing them to cool over-night. The liquor was removed from each flask by pouring off through a filter of copper gauze which retained all fine crystals: then the filter was reversed and liquor from the flask next in the series was poured in through the filter, thus rinsing the fine crystals back into the flask from which they had come. In this way, beginning with the head (most soluble) fraction, all the liquors were moved up one place at each crystallisation, and distilled water was added to the tail fraction. After several (usually three or four) crystallisations, the tail fraction disappeared and the head liquors were evaporated to form a new head fraction. Both series were systematically recrystallised after this fashion and by careful management the fractions were kept reasonably constant in size and number.

After the 60th crystallisation of both series, about 1150 crystallisations in all having been made in each, the extreme head and tail fractions were rejected and the heads A30 and B30, the tails A14 and B15 and the middle fractions A23 and B24 were taken for conversion into borax.

Preparation and Purification of Borax.

In order to obtain strictly comparable samples of borax the operations here described were carried out simultaneously on all six samples of boric acid.

About 120 g. of boric acid were added gradually to a slight excess (about 0·5%) over the calculated equivalent of pure sodium carbonate dissolved in about 200 c.c. of hot water. The sodium carbonate, originally very pure, had been twice recrystallised from water and was spectroscopically free from potassium. The solution was boiled to remove carbon dioxide, filtered whilst hot, and allowed to cool slowly without movement until about one-tenth of the borax had crystallised out. Then the clear liquor was poured off quickly into another vessel and further cooled with agitation, yielding a main crop of fine crystals of borax decahydrate, which were filtered with suction and immediately transferred to glass tubes for centrifugal drainage. The drainage tubes had in the bottom a thick pad of dry cotton wool covered with a wad of small filter papers and a porcelain disk, they were filled with the damp salt, closed by corks covered with filter paper, and centrifuged for

10 minutes at a speed of 2500 revolutions per minute. Thus the mother-liquor was very effectively removed.

The salt, contained in a platinum dish, was first dehydrated in an electrically-heated silica muffle, kept at 200—300° until intumescence ceased, and then fused by raising the temperature to about 700—800°. It thus formed a perfectly clear glass having only a faint blue tinge due to copper derived from the wire gauze filter mentioned above. Some difficulty was experienced at first in dissolving the borax glass in water: later, it was found that if the dish containing the fused glass were floated on cold water the mass developed numerous cracks which allowed water to penetrate the glass and greatly hastened solution. To dissolve the glass, the dish containing it was wholly immersed in water in a covered Durosil beaker heated over a Rose burner: solution was usually complete in about 2 hours.

After fusion, the borax was recrystallised four times from water in the manner already described, with centrifugal drainage of the main crop at each stage. Thus each sample was recrystallised five times in all, about one-tenth of the material in the head fraction and the same amount in the tail fraction being rejected each time. The crystallisations were done in covered Erlenmeyer flasks of Durosil, both these and the beakers having been thoroughly cleaned and boiled out with water for several days before use.

Tests for the chief impurities, carried out on the mother-liquors (head fraction) from each crystallisation, in which the impurities present tended to concentrate, gave a valuable indication of the purity of the main fraction without sacrifice of material therefrom.

Copper was estimated colorimetrically in an ammoniacal solution containing 1 g. of borax decahydrate; the standard solution of copper sulphate contained 1 part of copper in 100,000 parts, and in each case a "blank" test was made on the reagents alone. The head fractions from the earlier crystallisations contained traces of copper, but those from the final crystallisation of all six samples were absolutely free from copper.

Phosphate.—Mother-liquor equivalent to 1 g. of borax decahydrate was treated hot with nitric acid, ammonium nitrate, and ammonium molybdate. No trace of yellow ammonium phosphomolybdate was observed at any stage of the purification.

Sulphate.—The solution of borax was acidified with hydrochloric acid, treated with barium chloride solution, boiled, and kept, covered, over-night. The mother-liquor from the third recrystallisations showed traces of sulphate, but tests on the crystals gave negative results. Two further recrystallisations were made on each

sample and the mother-liquors from these gave negative results on the sulphate tests.

Chloride.—Nitric acid and silver nitrate were added to a solution containing 1 g. of crystallised borax. The third recrystallisation showed a slight opalescence; later tests were negative.

The final main fractions of borax were partly dehydrated by standing for 3 weeks over solid potassium hydroxide in desiccators and were then stored in stoppered bottles, capped to exclude dust.

Fusion of the pure borax was carried out in a platinum dish in the electrically heated muffle in a current of air, free from carbon dioxide and dried over solid caustic potash. The weight of borax taken was such as to yield from 3—10 g. of resultant "glass," as required, and the dehydration and fusion were conducted in the manner described above. When a clear glass was obtained, usually after about 1—1½ hours' fusion, a further period, in no case less than 2 hours, was allowed for complete dehydration. A shallow dish was used for fusion, and thus a large surface of borax was exposed. Samples of the molten glass were taken in two ways: (i) by pouring small beads on to a clean cold platinum surface; (ii) by dipping the bottom of a clean platinum crucible into the melt. In the latter case the glass adhered whilst hot, but, on cooling, cracked off in pieces weighing about 0·3 g. The samples were immediately transferred to, and kept in, a desiccator containing solid caustic potash.

As tests showed that when a bead of the glass weighing about 2 g. was kept on the balance pan for 3 days its weight did not change appreciably, this method of storage was evidently satisfactory. In every case the glass was weighed within 2 days after its fusion.

Method of Analysis.

Preliminary tests with a number of indicators showed that under the conditions of the titration methyl-red gave much the sharpest colour change, especially when the end-point chosen was slightly on the acid side. Under these conditions in $N/10$-borax solution, 2—3 drops of $N/100$-acid or alkali gave a considerable and sharp colour change.

During further tests which showed that the end-point in the borax titration was unaffected by moderate additions of boric acid and sodium chloride, it was observed that in a solution made from boric acid and salt, in the concentration which would be produced in the titration, the end-point was quite indefinite. This curious fact had no direct significance in the analyses now reported, but its further investigation at a future time is proposed.

The titrations were made by two distinct methods described below.

(a) *Using the weight burette.* Weighed beads of borax glass were dissolved to a 2% solution in water by boiling in a covered flask. After cooling, a quantity of $N/5$-acid, calculated to be 99% of that required for complete neutralisation, was added from the weight burette, a fixed volume of a stock solution of methyl-red was pipetted in, and the titration was completed by adding $N/100$-acid from a burette. The quantity of the latter required to give a match with a standard of definite pink shade could be ascertained with certainty within 0·1 c.c. Afterwards a measured excess of $N/100$-acid was added, then a measured excess of an equivalent solution of borax sufficient to make the solution distinctly yellow, and the end-point was again determined with $N/100$-acid.

(b) *By direct weighing of the acid solution.* As several of the earlier determinations showed unaccountable discrepancies, which might have been due to loss of borax (by spurting during solution) or of acid (by splashing when pouring in from the weight burette), a method of titration was devised to eliminate the possibility of such errors. The apparatus shown in Fig. 2 consisted of a 200 c.c. conical flask, A, and a reflux condenser, B, with a spray-trap, C, connected to A by a carefully ground joint.

TABLE III.

Data of Titrations of Borax Glass.

Sample number.		Vacuum wt. (g.) of borax glass.	Vacuum wt. (g.) of $N/5$-acid.	Calculated vacuum wt. (g.) of silver chloride.	Ratio: $\frac{\text{borax glass}}{\text{silver chloride}}$.	Atomic weight.
A14	1	1·99413	96·6881	2·83229	0·704068	10·961
	2	1·97982	95·9636	2·81107	0·704294	10·977
	3	1·93077	93·5412	2·74011	0·704632	11·001
	3*a*	0·81470	39·4923	1·15685	0·704239	10·973
	4	1·01079	48·9751	1·43463	0·704564	10·996
	5	1·04641	50·6956	1·48503	0·704638	11·002
	6	1·03879	50·3263	1·47421	0·704640	11·002
A24	1	1·00759	48·8258	1·43026	0·704481	10·990
	2	1·01246	49·1306	1·43919	0·703494	10·920
	3	2·14923	104·1576	3·05110	0·704412	10·985
	4	1·84391	89·3821	2·61828	0·704245	10·974
	5	1·90780	92·4578	2·70838	0·704407	10·985
	6	1·95549	94·7315	2·77498	0·704686	11·005
A30	1	1·21340	58·8361	1·72349	0·704036	10·958
	2	1·46470	70·9812	2·07926	0·704434	10·987
	3	1·41400	68·5272	2·00737	0·704403	10·985
	4	1·31097	63·5162	1·86059	0·704600	10·999
	5	0·67774	32·8309	0·96172	0·704717	11·007
	6	0·90300	43·6981	1·28005	0·705439	11·059
	7	1·01566	49·1406	1·43948	0·705574	11·069
	8	1·12262	54·2960	1·59050	0·705829	11·087
	9	1·22427	59·2639	1·73602	0·705215	11·043
	10	1·46529	70·9201	2·07747	0·705324	11·051

This apparatus was made in duplicate of Durosil glass and was cleaned with all the precautions already described. In using it, the required amount of $N/5$-acid was weighed in A against another similar flask as tare, the weighed borax was carefully slid down the dry side of the flask into the acid, the condenser was fitted, a little pure water was introduced into the spray trap, and the flask was heated gently over a Rose burner until the borax had completely dissolved (about 1 hour). After cooling, the contents of the bulbs and condenser were rinsed into the flask, these were removed, and the titration was completed with $N/100$-acid as described above. Working in this manner, the total volume of the solution titrated was little greater than that of the $N/5$-acid used.

Statement and Discussion of Results.

Table III gives the essential data of all the analyses made, and the values of the atomic weight of boron calculated therefrom. The results are evidently subject to errors (1) in the weight of borax taken, (2) in the volume of $N/100$-acid used, (3) in the weight of $N/5$-acid used in the titration, and (4) in the standardisation of the $N/5$-acid : the probable magnitude and effect of these errors are shown in Table IV.

TABLE IV.

Probable maximum value of error.	Corresponding variation in the atomic weight of boron.
(1) 0·1 C.c. of $N/100$-acid on 1 g. of borax-glass.....	±0·005
(2) 0·02 Mg. on 1 g. of borax	±0·001
(3) 0·5 Mg. on 50 g. of $N/5$-acid	±0·001
(4) Difference between standardisations : 1 in 15,000	±0·004
Total maximum error	±0·011

Making all due allowance for these errors, it would appear that the value obtained in each titration for the atomic weight of boron should not be in error by more than one or two units in the second decimal place, and there remain among the data considerable differences which must be otherwise explained.

After much worry had been caused by unaccountable and erratic variations in the atomic weight, it became apparent, as data accumulated, that the result was in many cases a function of the duration of fusion of the borax. Fortunately, precise records of the fusions were available : and their correlation with the results is shown in Table V. It is clear that a high atomic weight is always associated with a long period of fusion. The additional results on A30, Nos. 7, 8, 9, and 10, confirm this in a striking way.

The most probable inference is clear : a higher atomic weight corresponds with a lesser amount of acid used to neutralise a given weight of borax, hence to a lesser content of soda (Na_2O) in that

TABLE V.

Notes on Treatment of Samples.

Sample No.		Atomic weight.	Method of analysis.	Condition of fusion of borax glass.
A14	1	10·961		Molten 4—5 hours.
	2	10·977		Extra 5 g. of crystals added to residue (1). Fused 3½ hours. Both samples taken together.
	3	11·001	Simultaneous determinations by weight burette method.	
	3A	10·973		Extra crystals added to residue (2); fused 3 hours.
	4	10·996		Further amount of crystals dehydrated. Fused 6¾ hours.
	5	11·002	,,	
	6	11·002		
A24	1	10·990	Simultaneous determinations by weight burette method.	30 G. of crystals dehydrated to fusion; kept molten 2 hours.
	2	10·920		
	3	10·985	,,	Residue further fused 2 hours.
	4	10·974		
	5	10·985	,,	Residue from 3 and 4 further fused 2½ hours.
	6	11·005		
A30	1	10·958	Weight burette used.	20 G. of crystals dehydrated and fused 6 hours before sampling.
	2	10·987		
	3	10·985		
	4	10·999		
	5	11·007		
	6	11·059	Done in reflux-apparatus in $N/5$-acid.	Residue from (1—5) fused for 4 hours.
	7	11·069	,,	20 G. of crystals dehydrated and fused 10 hours.
	8	11·087		
	9	11·043	Done by weight burette method.	Residue from 7 and 8 fused for a further 7 hours.
	10	11·051		

borax: therefore, on fusion, borax loses soda and the extent of this loss increases with the duration of fusion.

Molten borax glass is known to volatilise, but previous workers have differed as to whether any decomposition takes place. Waldebott (*J. Amer. Chem. Soc.*, 1894, **16**, 410), as a result of experiments on the fusion of borax, was of the opinion that sodium tetraborate volatilised unchanged; he analysed the fused residue by treatment with ammonium fluoride and found no change in composition. The application of this method to an atomic weight determination was rejected, however, by Smith and van Haagen (*loc. cit.*). On the other hand, Leonard (*Chem. News*, 1898, **77**, 104), in criticism of the determinations of the atomic weight of boron by Armitage (*loc. cit.*), stated definitely that the residue obtained after fusion of borax required less standard acid for neutralisation than the original sample: this corresponds with a loss of soda. Smith and van Haagen assumed that acidic gases from burners had affected Leonard's borax, but no such explanation can be advanced in this case, since an electrically heated furnace was used to fuse the borax. Their own samples of borax glass were fused to constant weight

in a long-necked platinum flask and they concluded that the material condensed in the cooler part of the apparatus was identical in composition with the fused residue, and was pure sodium tetraborate. But their borax had been fused previously in an open crucible, one may infer for about the same time in the case of all samples, and the sample for analysis was taken from the upper portion of the main mass of glass which, by rotation, had been spread in a thin layer over the upper sides of the crucible and cooled quickly. Therefore the volatilisation of this sample in the flask without material change is quite consistent with its having already changed in composition during the open fusion in the way now observed.

Whatever the explanation may be, it seems clear that the borax ratios are subject to grave uncertainty, and the authors are definitely of opinion that all values for the atomic weight of boron determined by methods involving the weighing of fused borax should be entirely rejected in favour of those deduced from analyses of boron halides.

In summarising the present results it seems proper to discard A24, No. 2 for unaccountable discordance and A30, Nos. 6, 7, 8, 9, and 10, because in these cases the fusion was deliberately prolonged. The mean atomic weight deduced from the remaining determinations, B = 10·99, is in general agreement with the results previously obtained with fused borax, and is close to the results of Ramsay and Aston for the ratio $Na_2B_4O_7/2AgCl$, but differs widely from the results of determinations of the halide ratios.

For reasons which have been made clear, the authors attach no weight to this result.

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XXV.—*The Sulphur Compounds of Kimmeridge Shale Oil. Part I.*

By FREDERICK CHALLENGER, JAMES RICHARD ASHWORTH JINKS, and JOHN HASLAM.

THE oil obtained on distillation of the Kimmeridge shale of Dorset is characterised by a very high percentage of sulphur, which is stated to be 5—8% of the crude oil.* This has prevented its use

* References to other shale oils rich in sulphur are given by Demesse and Reaubourg, *Bull. Soc. chim.*, 1914, [iv], **15**, 625.

as a fuel, and although many attempts have been made to remove the sulphur compounds, these have been unsuccessful, excepting perhaps the recent hypochlorite process of Dunstan. The mode of combination of the sulphur has remained unknown (Perkin, *J. Inst. Pet. Tech.*, 1917, **3**, 227; Manfield, *loc. cit.*, 1916, **2**, 164; Craig and others, *loc. cit.*, 1918, **4**, 149).

Through the kindness of Mr. W. Hardy Manfield, who supplied us with several gallons of the crude oil, we have commenced an investigation with the object of identifying some of the sulphur compounds. The question of removing them on a commercial scale has not been considered. The only communication which contains any real information as to the ingredients of this shale oil was made by Williams (J., 1855, **7**, 97), who only examined the bases, which are sulphur-free. The peculiar odour of the oil seems to be due to these pyridine bases and to unsaturated hydrocarbons. In a typical experiment, 3 litres of the crude oil were distilled with steam until practically no more came over. The pale yellow oil (900 c.c.) was separated,* shaken with 200 c.c. of dilute hydrochloric acid (1 to 3), again separated, and the process repeated with 100 c.c. of the acid. The mixture was shaken for an hour and left over-night. The separated oil was shaken for an hour with 150 c.c. of 10% sodium hydroxide, dried over sodium sulphate, and fractionated three or four times at 15 mm. The table shows the fractions obtained and some analytical results :

Fraction.	B. p. at 15 mm.	Sulphur before $NaHSO_3$.	After $NaHSO_3$. S.	C.	H.	Total.
1	35—50°	10·67				
		10·83				
2	50—70	10·18	10·04	78·84	11·25	100·13
		10·14	10·04	79·03	11·08	100·15
			10·04	78·77	11·09	99·90
3	70—90	7·12				
		7·23				
4	90—110	6·38				
		6·46				
		6·39				
5	110—130	5·90				
6	130—145	7·04				

The first two fractions (95 c.c.; 140 c.c.) formed pale yellow oils of pleasant odour which on analysis showed the presence of traces of oxygen. They were therefore separately shaken with saturated sodium bisulphite solution, separated, washed, and analysed. The bisulphite extracts with sodium carbonate yielded 1 c.c. of ketones, b. p. 130—150°, which readily combined with semicarbazide.

* The water (9 litres) was extracted with ether, bases and phenols were removed as before, and the residue was added to the main bulk.

After four rectifications of fraction 1 at the ordinary pressure (no hydrogen sulphide was evolved), fractions were obtained of which the first (b. p. 60—110°) contained 14·07, and the last (b. p. above 150°), 7·82% of sulphur. On standing for some weeks, resin was deposited, doubtless arising from olefines or diolefines. On redistillation, water was formed and a sharp odour observed, probably due to unsaturated aldehydes arising from decomposition of some oxidation product.

Removal of Sulphur from Fraction, b. p. 60—110°.—Five c.c. were slowly added to 25 c.c. of sulphuric acid at — 15°. A dark-red colour developed, as with all fractions of the oil. The mixture was well shaken, and after 1½ hours the oil was separated, washed with water, and found to be free from sulphur. It gave no indophenin reaction nor any colour with sulphuric acid, was stable to cold aqueous permanganate, and had a strong odour of toluene. After nitration with sulphuric and nitric acids at 100°, the product slowly solidified to white needles containing nitrogen (m. p. and mixed m. p. with 2 : 4-dinitrotoluene, 71°).

Oxidation of the Fraction, b. p. 50—70°/15 *mm.*—(a) *With potassium permanganate.* The oil was sealed in a bulb which was added to 200 c.c. of 2% aqueous potassium permanganate, and broken by shaking. After 10 hours' shaking and addition of more permanganate till decoloration ceased, the solution was filtered, acidified with hydrochloric acid, and precipitated with barium chloride, excess of permanganate being removed with alcohol: (1) 0·4462 gave 0·2450 $BaSO_4$; S = 7·54. (2) 0·5106 gave 0·2830 $BaSO_4$; S = 7·61. (3) 0·7808 gave 0·4264 $BaSO_4$; S = 7·50. In (3) the solution was evaporated with nitric acid to remove any oxalates.

(b) *With nitric acid.* About 0·5 g. was shaken for 4 hours with 12 c.c. of water and 5 c.c. of fuming nitric acid and evaporated with hydrochloric acid and salt: 0·5080 gave 0·2695 $BaSO_4$; S = 7·28. 0·5110 gave 0·2766 $BaSO_4$; S = 7·43. About 75% of the total sulphur is obtained as sulphuric acid. This would indicate that alkyl sulphides and mercaptans are not, at any rate, the chief sulphur compounds present, whilst the cyclic polymethylene sulphides also form stable sulphones on oxidation (Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1, 880).

Identification of 2-Methylthiophen in a Fraction, b. p. 80—110°.—The fraction (11 g.), mercuric acetate (80 g.), and 230 c.c. of water were shaken for 15 hours. The precipitate (36 g.), which contained much mercurous acetate due to the presence of olefines, was extracted three times with hot alcohol. The insoluble residue decomposed about 225°. 16 G. were distilled with 60 c.c. of hydro-

chloric acid (1 : 2), giving about 3 c.c. of a colourless oil. This had a pure aromatic odour and gave a strong indophenin reaction. With excess of bromine water, long needles, m. p. 86—87°, were obtained. Tribromo-2-methylthiophen melts at 87°, but when mixed with the corresponding 3-methyl derivative, non-separable mixed crystals, m. p. 74°, are obtained (Meyer, *Ber.*, 1885, **18**, 544). 3-Methylthiophen would therefore seem to be absent.

2-*Methylthiophenmercurichloride*, $CH_3 \cdot C_4H_2S \cdot HgCl$.—One c.c. of the regenerated oil was shaken with 10 c.c. of alcohol, 100 c.c. of saturated mercuric chloride solution, and 30 c.c. of 33% sodium acetate solution. The precipitate (2·6 g.) was free from mercurous chloride.* Recrystallised from hot alcohol and then from acetone, it had m. p. 194—195° with slight previous sintering; but when placed in the bath at 190°, its m. p. was 202°. Repeated experiments gave no depression of the m. p. on admixture with authentic 2-methylthiophenmercurichloride. The compound was converted to mercury 2 : 2′-dimethyldithienyl, $(CH_3 \cdot C_4H_2S)_2Hg$, by the method of Steinkopf (*Annalen*, 1921, **424**, 40); m. p. and mixed m. p. 160°. This was converted by mercuric bromide into 2-methylthiophenmercuribromide (Steinkopf, *loc. cit.*); m. p. and mixed m. p. 178°. All these mercury derivatives of thiophen homologues were shown by Steinkopf to sinter slightly before melting. The non-depression of m. p. was, however, very definite. The m. p. of 2-methylthiophenmercurichloride was strongly depressed on admixture with the corresponding thiophen compound.

Identification of Thiophen.—Another specimen of the oil purified as before gave fractions, b. p. 77—83° and 83—93°. With mercuric chloride and sodium acetate these gave mercurous chloride (due to olefines) and traces of a solid which, on repeated crystallisation from alcohol and acetone, gave a strong indophenin reaction and was identified as thiophenmercurichloride by its m. p. and mixed m. p. (180—181°). It strongly depressed the m. p. of 2-methylthiophenmercurichloride.

The presence of thiophen derivatives in the oil explains its behaviour on oxidation. In some cases, Meyer ("Die Thiophen Gruppe," pp. 55, 204) obtained very bad yields of carboxylic acids on oxidation of the alkylthiophens, owing to almost complete decomposition. We find that cold 2% aqueous potassium permanganate completely oxidises thiophen to sulphuric acid, although Angeli and Alessandri (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 314) state that it is stable to alcoholic permanganate.

Our results are in general agreement with those of other workers. Scheibler (*Ber.*, 1915, **48**, 1815; 1916, **49**, 2595; 1919, **52**, 1903)

* Due to previous removal of olefines with mercuric acetate.

examined shale oils rich in sulphur. His method of purification was very complicated, but from a fraction of b. p. 170–180°/360 mm. he obtained with acetyl chloride and aluminium chloride a ketone, possibly propylacetothienone, $C_4H_2PrS{\cdot}COMe$, and analysed the semicarbazone. Pfaff and Kreutzer (*Z. angew. Chem.*, 1923, **36**, 437) identified 2-methylthiophen in a fraction of lignite tar by conversion into 2-methylacetothienone.

THE UNIVERSITY, MANCHESTER. [*Received, November 20th*, 1924.]

XXVI.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part V. The Synthesis of Cyanidin Chloride and of Delphinidin Chloride.*

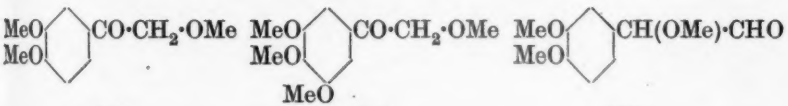
By DAVID DOIG PRATT and ROBERT ROBINSON.

IN Part II (J., 1923, **123**, 750), it was shown that ω-methoxyacetoveratrone (I) can be obtained by the methylation of ω-hydroxyacetoveratrone by means of silver oxide and methyl iodide. The oily product yielded isomeric semicarbazones, $C_{12}H_{17}O_4N_3$, (*a*) m. p. 205°, and (*b*) m. p. 168°, whilst condensation with β-resorcylaldehyde in presence of hydrogen chloride gave rise to a pyrylium salt characterised as the ferrichloride, $C_{18}H_{17}O_5Cl_4Fe$, m. p. 156°. The unsatisfactory character of the process is emphasised in the memoir quoted and as a preliminary to an attempt to synthesise cyanidin chloride it was clearly essential to work out an entirely novel method of preparation of ω-methoxyacetoveratrone. We desired to proceed from veratric acid in order that the process might subsequently be applied to the trimethyl ether of gallic acid and so lead to a synthesis of delphinidin salts. After unsuccessful trials in other directions, *e.g.*, in attempting the decomposition of diazoacetophenones by methyl alcohol, the solution of the problem was found in an application of the synthesis of acetophenone from benzoyl chloride by way of ethyl benzoylacetate. The action of sodium on ethyl methoxyacetate leads to the sodio-derivative of ethyl αγ-dimethoxyacetoacetate, $MeO{\cdot}CH_2{\cdot}CO{\cdot}CH(OMe){\cdot}CO_2Et$, which readily yields *C*-aroyl derivatives. Ethyl αγ-dimethoxy-α-benzoylacetoacetate was decomposed by boiling dilute sulphuric acid with formation of phenylglyoxal in poor yield, but when it was subjected to the prolonged action of cold dilute potassium hydroxide and the mixture was subsequently boiled, ω-methoxyacetophenone (Part II, p. 748) was obtained in accordance with the scheme :—

$$\begin{matrix} CO\cdot CH_2\cdot OMe \\ Ph\cdot CO\cdot C(OMe)\cdot CO_2Et \end{matrix} \xrightarrow[+3KOH]{} Ph\cdot CO\cdot CH_2\cdot OMe + MeO\cdot CH_2\cdot CO_2K + K_2CO_3 + EtOH.$$

In a similar manner, ω : 4-dimethoxyacetophenone (Part II, p. 750) was derived from anisic acid, and the product of the interaction of ethyl sodio-αγ-dimethoxyacetoacetate and veratroyl chloride in dry ethereal solution yielded ω-methoxyacetoveratrone on careful hydrolysis with alkali. The analogous preparation of ω : 3 : 4 : 5-tetramethoxyacetophenone (II) offered no difficulty.

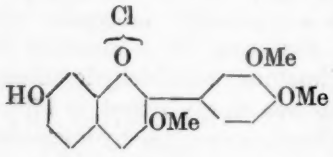
Pure ω-methoxyacetoveratrone is a crystalline substance which gives a single semicarbazone, m. p. 178°, and this is identical with the previously described veratrylmethoxyacetaldehydesemicarbazone-b, the melting point of which was slowly raised to 178° by repeated crystallisation. Veratrylmethoxyacetaldehydesemicarbazone-a, m. p. 205°, was the more sparingly soluble of the isomerides and its melting point is not raised on recrystallisation. This substance is plainly the semicarbazone of α : 3 : 4-trimethoxyphenylacetaldehyde (III), and the formation of the latter in the methylation of veratroylcarbinol is noteworthy.



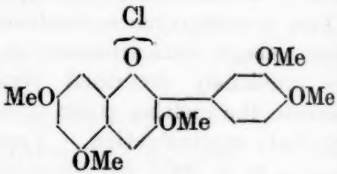
(I.) (II.) (III.)

ω-Methoxyacetoveratrone and ω : 3 : 4 : 5-tetramethoxyacetophenone are much more soluble in cold than in hot water, a property which doubtless indicates the formation and decomposition of hydrates. The former ketone on condensation with β-resorcylaldehyde in presence of hydrogen chloride yields trimethylfisetinidin chloride (IV), and the derived ferrichloride, m. p. 156°, is identical with the substance obtained as mentioned above. 2-Hydroxy-4 : 6-dimethoxybenzaldehyde and ω-methoxyacetoveratrone condense under the agency of hydrogen chloride in ethereal solution with formation of cyanidin chloride pentamethyl ether (V), and this salt is demethylated by means of boiling hydriodic acid in presence of phenol with formation of cyanidin iodide. Cyanidin chloride (VI) was prepared from the iodide in the usual manner and the product exhibited in every detail the properties of cyanidin chloride of natural origin as described by Willstätter and Everest (*Annalen*, 1913, **401**, 189) and Willstätter and Nolan (*ibid.*, 1915, **408**, 13). A direct comparison of the synthetical material with an authentic specimen disclosed no differences existing between them. The production of cyanidin chloride by the reduction of quercetin in acid solution (Willstätter and Mallison, *Sitzungsber. Preuss.*

Akad. Wiss., 1914, 769) constitutes in one sense a synthesis of the substance, and furthermore Willstätter and Kindler, in 1919, made a communication to the Münchner Chemische Gesellschaft concerning experiments which they had conducted on the application of the Willstätter-Zechmeister pelargonidin synthesis to the case of cyanidin ("Wissenschaftliche Forschungsberichte, III, Organische Chemie," R. Pummerer, 2nd Edition, 1923, 150). The details of the results obtained are not yet available.*



(IV.)



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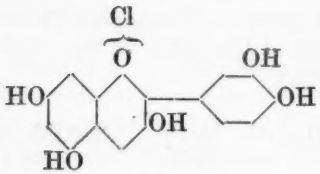
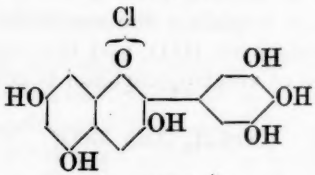


(VI.)



(VII.)

The synthesis of delphinidin chloride (VII) followed the lines of that of cyanidin chloride, delphinidin chloride hexamethyl ether being obtained from hydroxydimethoxybenzaldehyde and $\omega : 3 : 4 : 5$-tetramethoxyacetophenone (II). As shown in the experimental portion on page 174, there can be no doubt as to the identity of the synthetical product, obtained on demethylation, with that of natural origin.

EXPERIMENTAL.

Ethyl αγ-Dimethoxyacetoacetate.—Ethyl chloroacetate (122 g.) was gradually added with cooling and shaking to a solution of sodium methoxide (from 23 g. of sodium) in anhydrous methyl alcohol (200 c.c.). The mixture was refluxed until neutral, most of the alcohol then removed, and the residue mixed with brine and ether. The dried ethereal solution on fractionation yielded 85 g. of ethyl methoxyacetate, b. p. 131°.† Sodium (8 g.), cut in thin slices,

* Willstätter, Zechmeister, and Kindler have now published their work (*Ber.*, 1924, **57**, [*B*], 1938).

† This substance can also be obtained by the hydrolysis of methoxyacetonitrile by Pinner's method. Ethyl ethoxyacetate (Henry, *Ber.*, 1871, **4**, 706); ethyl αγ-diethoxyacetoacetate (Conrad, *Ber.*, 1878, **11**, 58; Erlenbach, *Annalen*, 1892, **269**, 28). In order to avoid the possibility of replace-

was added in one portion to ethyl methoxyacetate (100 g.); the reaction, which soon commenced, was controlled by cooling in melting ice when necessary. The thick syrup which resulted was treated with 50% acetic acid (45 c.c.) and saturated brine and extracted with ether. The ethereal layer was separated, washed with aqueous sodium carbonate, dried with anhydrous sodium sulphate, and distilled; 40 g. of a colourless oil, b. p. 130°/15 mm., were obtained (Found: C = 50·4; H = 7·4. $C_8H_{14}O_5$ requires C = 50·5; H = 7·4%). This ester is moderately readily soluble in water, and its alcoholic solution gives a violet coloration with ferric chloride, the shade being bluer than that developed by ethyl acetoacetate under similar conditions.

ω : 4-*Dimethoxyacetophenone.*—In the first place, experiments on the hydrolysis of the condensation product from ethyl sodio-αγ-dimethoxyacetoacetate and benzoyl chloride were made. After boiling with dilute sulphuric acid and distillation in a current of steam, a yellow distillate was obtained, and this by suitable treatment yielded phenylglyoxaldiphenylhydrazone, m. p. 152°. When, however, the product was boiled with dilute aqueous sodium hydroxide, ω-methoxyacetophenone was obtained in small yield and identified as the semicarbazone, m. p. 85°. ω : 4-Dimethoxyacetophenone may be obtained in the following manner: Sodium (2·7 g.) was granulated under toluene, washed with ether, suspended in anhydrous ether (150 c.c.), and ethyl αγ-dimethoxyacetoacetate (22·3 g.) gradually added. A sodio-derivative separated from the solution and, when the sodium had disappeared, anisoyl chloride (20 g.) was added in one portion. A gentle reaction occurred and after 1 hour the process was completed by heating on the steam-bath under reflux during 4 hours. Next day water was added, the ethereal layer dried over sodium sulphate, and after removal of the solvent 35 g. of a pale yellow oil remained. The whole was agitated for 12 hours with 2·5% aqueous potassium hydroxide (500 c.c.), and the liquid then boiled for 3 hours, cooled, nearly saturated with potassium carbonate, and extracted with ether; 7·5 g. of the ketone, m. p. 40°, were obtained.

On condensation with 6-aminopiperonal in alcoholic solution by means of potassium hydroxide, ω : 4-dimethoxyacetophenone yields

ment of the ethyl group of the esters by methyl and the production of mixtures Mr. N. L. Matthews has employed methyl chloroacetate and condensed this with sodium methoxide in dry methyl-alcoholic solution in the cold. Methyl chloroacetate (108 g.) yielded methyl methoxyacetate (70 g.), b. p. 129°/754 mm. Methyl methoxyacetate (100 g.) reacted with sodium (9 g.) to give a product from which *methyl αγ-dimethoxyacetoacetate*, b. p. 129°/17 mm., could be isolated (Found: C = 47·5; H = 7·1. $C_7H_{12}O$ requires C = 47·7; H = 6·8%). The yield was 40—50% of that required by theory.

3-*methoxy*-6 : 7-*methylenedioxy*-2-(4-*methoxyphenyl*)*quinoline*, which crystallises from methyl alcohol in colourless laminæ, m. p. 152°.

ω-*Methoxyacetoveratrone* (I).—Ethyl αγ-dimethoxyacetoacetate (36·2 g.) was gradually added to finely granulated sodium (4·4 g.) suspended in anhydrous ether (225 c.c.). Formation of the sodio-derivative appeared to be complete after an hour, and a solution of distilled veratroyl chloride (38 g.) in ether (150 c.c.) was introduced, causing a mild reaction. The mixture was gently heated on the steam-bath for 2 hours, allowed to remain over-night, and heated during a further 2 hours. After washing with water, drying, and evaporating the ether, there remained 63 g. of a pale orange, viscous liquid which could not be crystallised. The whole product was hydrolysed by vigorous agitation for 9 hours with cold 2·5% aqueous potassium hydroxide (800 c.c.) and finally by boiling the clear solution for 5 hours. The ketone was isolated by extraction with ether after the addition of much potassium carbonate and purified by distillation; 22 g. of an oil, b. p. 190°/15 mm., were obtained which solidified. The substance crystallises from light petroleum containing a little benzene in colourless prisms, m. p. 62° (Found: C = 63·1; H = 6·8. $C_{11}H_{14}O_4$ requires C = 62·9; H = 6·7%). When a little of this substance is melted under water and the mixture cooled, a clear solution is obtained from which the ketone may be precipitated as an oil either by heating or by the addition of an alkali carbonate or hydroxide. The substance is very readily soluble in organic solvents with the exception of light petroleum. On condensation with 6-aminopiperonal, it yields 3-*methoxy*-6 : 7-*methylenedioxy*-2-(3 : 4-*dimethoxyphenyl*)*quinoline*, which crystallises from ethyl alcohol in slender needles, m. p. 155°, and exhibits a violet fluorescence in alcoholic solution.

Fisetinidin Chloride Trimethyl Ether (IV).

A slow stream of hydrogen chloride was passed through an ice-cold solution of β-resorcylaldehyde (2 g.) and ω-methoxyacetoveratrone (3 g.) in dry ether (40 c.c.), when the liquid became yellow and then red and crystallisation commenced after 20 minutes. The passage of the gas was discontinued after 30 minutes and after several hours the pyrylium salt, which exhibited an intense green lustre, was collected, washed with ether, and dried (3·4 g.). The ethereal mother-liquors were washed with dilute hydrochloric acid and a ferrichloride (0·2 g.) was precipitated. This derivative crystallises from acetic acid in reddish-brown needles, m. p. 156°, and its properties are identical with those of the ferrichloride previously prepared from the product of methylation of veratroylcarbinol (*loc. cit.*). Fisetinidin chloride trimethyl ether dissolves in

hot 7% hydrochloric acid to an orange-red solution and separates completely on cooling in reddish-brown, prismatic needles exhibiting a green reflex (Found in material dried in a vacuum: C = 56·1; H = 5·3. $C_{18}H_{17}O_5Cl,2H_2O$ requires C = 56·2; H = 5·5%). This salt darkens at 135° and decomposes at 188—189°. It is reddish-violet by transmitted light and makes a violet smear on paper. Its alcoholic solutions are intensely reddish-violet and the orange solution in concentrated sulphuric acid exhibits a green fluorescence. Sparingly soluble in cold water, it dissolves on warming to an orange-red solution which on dilution is rapidly decolorised with formation of the ψ-base. The violet colour-base is precipitated when sodium acetate is added to a moderately concentrated aqueous solution of the salt, but if a dilute solution is treated with sodium acetate the appearance of the violet colour is transient and the ψ-base is obtained. *iso*Amyl alcohol extracts the salt completely from an acid aqueous solution and the addition of sodium acetate to the red alcoholic extract gives a violet solution the colour of which fades. The oxonium salt is regenerated from solutions of the colour-base and ψ-base by the addition of hydrochloric acid.

Cyanidin Chloride Pentamethyl Ether (V).

In order to obtain good results in this preparation, it is very necessary that the materials employed should be pure. Hydrogen chloride was passed for 1 hour through a solution of 2-hydroxy-4:6-dimethoxybenzaldehyde (4·5 g.) and ω-methoxyacetoveratrone (5·2 g.) in ether (50 c.c.). The solution quickly became crimson and crystallisation of the product was induced by scratching after 30 minutes from the commencement. The tube containing the mixture and a dish containing solid potassium hydroxide were together covered by a bell-jar and after several hours the salt was collected, washed with ether, and dried (5·5 g.). The salt crystallises from alcohol containing a little hydrogen chloride in small, red needles, m. p. 152°, which in mass exhibit an old-gold sheen, but give a chocolate-brown smear on paper (Found, in material dried in a vacuum over phosphoric oxide and potassium hydroxide: C = 51·7; H = 5·9; Cl = 14·9. $C_{20}H_{21}O_6Cl,HCl,2H_2O$ requires C = 51·6; H = 5·6; Cl = 15·2%). The same *dichloride* crystallised from a mixture of alcohol and concentrated aqueous hydrochloric acid in slender needles, m. p. 152° (Found: C = 51·5; H = 5·5; Cl = 15·4%). From 7% aqueous hydrochloric acid, the salt separates in long, orange-brown needles which form a crystalline crust exhibiting a green reflex (Found, in material dried in a vacuum: C = 53·2; H = 6·0. $C_{20}H_{21}O_6Cl,3H_2O$ requires C = 53·7; H = 6·0%). The substance is readily soluble in the simple

alcohols to reddish-violet solutions the colour of which fades on dilution with water and can then be restored by the addition of a mineral acid. The *ferrichloride* crystallises from acetic acid, in which it is very sparingly soluble, in reddish-brown, prismatic needles, m. p. 194—200° (decomp.), exhibiting a bronze lustre. The chloride is insoluble in chloroform, but this derivative is moderately readily soluble and when the hot saturated solution is rapidly concentrated to one-quarter of its bulk the ferrichloride separates in microscopic needles exhibiting an intense green lustre.

Cyanidin Chloride (VI).

The foregoing pentamethyl ether (3·2 g.) and phenol (15 g.) were added to hydriodic acid (180 c.c.; *d* 1·7) and the mixture was boiled for 30 minutes in an atmosphere of carbon dioxide. Water (2 vols.) and much ether were added to the cooled solution and, on standing, glistening needles with a bright green reflex separated. The substance (1·8 g.) had properties identical with those of cyanidin iodide prepared by the demethylation of paeonidin chloride of natural origin (Willstätter and Nolan, *Annalen*, 1915, **408**, 136). The iodide (3 g.) was thoroughly ground with aqueous sodium acetate, the bluish-violet colour-base separated, thoroughly washed, and heated to boiling with 3% aqueous hydrochloric acid (100 c.c.) in presence of a trace of silver, and filtered, 50 c.c. more 3% hydrochloric acid being used for washing. Concentrated hydrochloric acid (50 c.c.) was added and, on standing, the dark red solution deposited the salt completely in masses of short, reddish-brown prisms that had a green lustre (Found: C = 52·5; H = 4·1. $C_{15}H_{11}O_6Cl,H_2O$ requires C = 52·8; H = 3·8%). This product showed all the characteristic reactions of cyanidin chloride, and a direct comparison with a specimen of the substance of natural origin disclosed no difference in properties of any kind. The behaviour on heating, appearance of the crystals under the microscope, formation of colour-base and ψ-base, solubilities in aqueous and alcoholic acid solutions, colour of acid solutions, absorption spectrum of the solution in ethyl alcohol, and the reactions with ferric chloride, sodium carbonate, sodium acetate, potassium acetate in alcoholic solution, lead acetate and Fehling's solution were all examined. Willstätter and Everest (*loc. cit.*) state that cyanidin on oxidation with hydrogen peroxide yields a yellow, crystalline product closely resembling a flavonol colouring matter. There is, however, no clear evidence that quercetin can be obtained by the oxidation of cyanidin and furthermore it is remarkable that no chromone or chromonol derivative has yet been prepared by oxidising a benzopyrylium salt. We have made numerous experi-

ments with the object of achieving this transformation, but any definite products isolated have been either carboxylic acids or coumarin derivatives. This investigation proceeds.

ω : 3 : 4 : 5-*Tetramethoxyacetophenone* (II).—Sodium (2·5 g.), granulated under toluene and washed with ether, was suspended in ether (120 c.c.), and ethyl αγ-dimethoxyacetoacetate (20 g.) slowly added. When the formation of the sodio-derivative appeared to be complete, an ethereal solution of trimethylgalloyl chloride (24·5 g.) was added in one portion, and the mixture heated gently on the steam-bath for 8 hours. The product was isolated (34 g.) and shaken for 12 hours with 2·5% aqueous potassium hydroxide. The solution was boiled for 4 hours, and the ketone isolated as in the case of ω-methoxyacetoveratrone. The yield was 9 g. of a colourless oil, b. p. 212°/15 mm., which solidified in contact with light petroleum. The substance crystallises from benzene–light petroleum in colourless needles, m. p. 54°, and closely resembles ω-methoxyacetoveratrone (Found : C = 60·0; H = 6·3. $C_{12}H_{16}O_5$ requires C = 60·0; H = 6·6%). The *semicarbazone* crystallises from aqueous alcohol in long, colourless needles, m. p. 158°.

3-*Methoxy*-6 : 7-*methylenedioxy*-2-(3 : 4 : 5-*trimethoxyphenyl*)*quinoline* crystallises from ethyl alcohol in colourless needles, m. p. 159°, and exhibits a violet fluorescence in alcoholic solution. Its salts, *e.g.*, the sparingly soluble *hydrochloride*, are yellow. The *methosulphate* is orange-yellow and it is evident from a comparison of this substance with the intensely coloured delphinidin chloride hexamethyl ether that the quinolinium and benzopyrylium nuclei function quite differently as chromophores. It may well be that the methoxyl groups are able to decentralise the cationic valency of the pyrylium nucleus and so produce changes of orbits of electrons owing to recurrent redistribution of the charge, whilst, on the other hand, the powerfully basic quinolinium nucleus is able to ignore the claims of the weak auxochromes. We are thus led to anticipate that the aminophenylquinolinium salts will resemble tinctorially the related hydroxyphenylbenzopyrylium salts and it is hoped that an experimental test of this point will be made.

Delphinidin Chloride Hexamethyl Ether (corresponding with VII).

Hydrogen chloride was passed through an ice-cold solution of ω : 3 : 4 : 5-tetramethoxyacetophenone (4 g.) and 2-hydroxy-4 : 6-dimethoxybenzaldehyde (3 g.) in dry ether (50 c.c.), crystallisation of the product in crimson needles and prisms having a dark green reflex occurring after about 1 hour. Next day, the salt (4 g.) was collected and a further quantity (0·7 g.) was obtained from the ethereal mother-liquor. The substance crystallises from alcohol

containing a trace of hydrogen chloride in long, red needles, m. p. 163—164° (Found, in material dried in a vacuum: C = 58·5; H = 5·8. $C_{21}H_{23}O_7Cl,0{\cdot}5H_2O$ requires C = 58·4; H = 5·6%). The substance exhibits a green lustre and is reddish-violet by transmitted light. It is readily soluble in the simple alcohols and moderately soluble in chloroform to a reddish-violet solution. The dark red colour of the solution in water rapidly fades and an almost colourless ψ-base is precipitated. Faintly acid solutions are also decolorised on great dilution, but addition of acid restores the colour of the pyrylium salt. The *ferrichloride* crystallises from glacial acetic acid in brownish-red needles which have a dark green appearance in mass. This derivative, m. p. 169—170°, is readily soluble in acetone, chloroform, or the simple alcohols. The *sulphate* crystallises from dilute sulphuric acid in slender, red needles with green reflex, m. p. 225° (decomp.).

Delphinidin Chloride (VII).

Delphinidin chloride hexamethyl ether (3·0 g.) was demethylated by means of a boiling mixture of hydriodic acid (180 c.c.; *d* 1·7) and phenol (15 g.) during 30 minutes, a slow current of carbon dioxide being passed through the containing vessel. The cooled liquid deposited clusters of long, pointed, brown needles together with some squat prisms, and these were collected, washed with ether, and dried (2·0 g.). The iodide was converted into chloride by treatment at 60° with silver chloride in alcoholic solution in a silver-mirrored vessel. The filtered solution was mixed with an equal volume of concentrated hydrochloric acid, and the amorphous precipitate so obtained allowed to remain, when it slowly became resolved into a mass of microscopic needles. The substance was isolated and crystallised by solution in 5% hydrochloric acid and addition of 30% acid to the filtered solution so as to make the concentration of hydrochloric acid about 25%. The brown, crystalline mass was dried in a vacuum (Found: C = 49·4; H = 4·0. $C_{15}H_{11}O_7Cl,1{\cdot}5H_2O$ requires C = 49·4; H = 3·8; H_2O = 7·4%). According to Willstätter and Weil (*Annalen*, 1916, **412**, 178), delphinidin chloride crystallises from hydrochloric acid of 20% or greater concentrations with $1{\cdot}5H_2O$, which is completely lost in a vacuum. Our product did not behave in this way, but the circumstance was an accident, since when the material was powdered and again exposed to a vacuum it lost 7·6%. The anhydrous salt does not melt below 350°. The hydrates containing $1H_2O$, $2H_2O$, and $4H_2O$ have been prepared by the methods devised by Willstätter and Weil in order to observe the crystalline forms, which were found to agree with the descriptions of these authors.

The absorption spectrum of an alcoholic solution of the chloride, the formation of the ψ-base, the behaviour of aqueous and acid solutions on shaking with ether, ethyl acetate and *iso*amyl alcohol, the reactions with ferric chloride in aqueous and alcoholic solutions and with sodium carbonate, sodium bisulphite, lead acetate, and Fehling's solution were all examined with results identical with those described in the case of delphinidin chloride of natural origin by Willstätter and Mieg (*Annalen*, 1915, **408**, 61) and Willstätter and Weil (*loc. cit.*). We were not able to make a direct comparison, but the properties of delphinidin chloride are so characteristic and have been recorded in such detail that we can entertain no doubt as to the identity of the synthetical product with that obtained by the hydrolysis of the pigments of the wild purple larkspur and the blue-black pansy.

One of us (D. D. P.) desires to thank the Carnegie Trust for the Universities of Scotland for a Fellowship which has enabled him to take part in this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, November 3rd*, 1924.]

XXVII.—*Synthesis of certain Higher Aliphatic Compounds. Part I. A Synthesis of Lactarinic Acid and of Oleic Acid.*

By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

THIS investigation originated in a desire to develop methods which could be applied to the synthesis of the naturally occurring, unsaturated fatty acids and attention was concentrated in the first place on attempts to synthesise oleic acid. An examination of the literature shows that this acid has been obtained from 10-ketostearic acid,* $CH_3 \cdot [CH_2]_7 \cdot CO \cdot [CH_2]_8 \cdot CO_2H$, by reduction to hydroxystearic acid followed by conversion to iodostearic acid and treatment with alcoholic potassium hydroxide (see p. 179). It therefore became an object to devise a process for the preparation of acids of the form $R \cdot [CH_2]_m \cdot CO \cdot [CH_2]_n \cdot CO_2H$, which should be applicable to a case such that $R \cdot [CH_2]_m I$ cannot be readily converted into an organo-zinc or magnesium derivative. After numerous trials in other directions, it was found that ethyl sodio-*n*-heptylmalonate and 9-carbethoxynonoyl chloride condensed in ethereal solution to a product which

* The carboxyl group of stearic acid is numbered 1 in this communication in order to avoid confusion with the Geneva nomenclature. This system has been frequently adopted n recent literature.

gave a very small yield of 10-ketostearic acid on prolonged hydrolysis with boiling 1% aqueous oxalic acid. A considerable improvement was effected by starting with ethyl acetoacetate instead of ethyl malonate. Ethyl sodio-2-acetylnonoate and 9-carbethoxynonoyl chloride were brought into reaction in ether, and the resulting ester, $CH_3 \cdot [CH_2]_6 \cdot CAc(CO_2Et) \cdot CO \cdot [CH_2]_8 \cdot CO_2Et$, was cautiously hydrolysed at first by cold dilute alkali, then by boiling dilute sulphuric acid and finally by boiling dilute aqueous sodium hydroxide. The sparingly soluble, crystalline sodium salt of 10-ketostearic acid separated on cooling the solution. This acid melts at 83° and the product of the action of sulphuric acid and water on stearolic acid, after a wasteful process of purification, melts at the same temperature, alone or mixed with the synthetic specimen. It is probable that the isomeride accompanying 10-ketostearic acid in the crude material derived from stearolic acid is 9-ketostearic acid and we are engaged in the preparation of this substance in order to determine the proportions in which the acetylenic bond is hydrated in the two possible directions. The synthesis of oleic acid by way of 10-ketostearic acid and 10-iodostearic acid affords a proof that the double bond is in the position $\Delta^{9:10}$ or $\Delta^{10:11}$ and in order to eliminate the latter alternative we are engaged in an attempt to synthesise stearolic acid. We have found that this acid may be reduced to oleic acid by means of zinc dust and hydrochloric acid in presence of titanous chloride in acetic acid solution. Elaidic and stearic acids are not produced under the conditions described (p. 177) and the reaction indicates that oleic acid has the *cis*-configuration. The addition of hydrogen iodide to stearolic acid has been previously shown to lead to isomeric iodoelaidic acids which can be transformed into elaidic acid (Arnaud and Posternak, *Compt. rend.*, 1910, **150**, 1130, 1525).

In the course of investigations on the constituents of certain fungi, Bougault and Charaux found that several species of *Lactarius* contained a ketostearic acid, termed lactarinic acid, in the free state (*Compt. rend.*, 1911, **153**, 572, 880). The results obtained by applying the Beckmann transformation to the oxime of lactarinic acid showed that the substance must be 6-ketostearic acid and we have now confirmed this conclusion by synthesis. Ethyl sodio-2-acetyl-*n*-tridecoate and 5-carbethoxyvaleryl chloride react in ethereal solution so as to produce the ester

$$CH_3 \cdot [CH_2]_{10} \cdot CAc(CO_2Et) \cdot CO \cdot [CH_2]_4 \cdot CO_2Et,$$

which by graduated hydrolysis yields lactarinic acid,

$$CH_3 \cdot [CH_2]_{11} \cdot CO \cdot [CH_2]_4 \cdot CO_2H.$$

We are greatly indebted to Professor Bougault for a specimen of the acid of natural origin, and a careful comparison proved the identity

of this with the synthetical product. At the suggestion of Professor H. S. Raper, we have also synthesised 4-ketopalmitic acid in order to render possible a direct comparison with a substance prepared by the oxidation of palmitic acid. In this case, ethyl sodio-2-acetyl-*n*-tridecoate and 3-carbomethoxypropionyl chloride gave the ester $CH_3{\cdot}[CH_2]_{10}{\cdot}CAc(CO_2Et){\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2Me$, and by hydrolysis the desired keto-acid, $CH_3{\cdot}[CH_2]_{11}{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$.

Experimental.

Reduction of Stearolic Acid to Oleic Acid.—Hydrochloric acid (50 c.c. of 40%) was slowly added to a gently boiling mixture of acetic acid (30 g.), aqueous titanous chloride (10 g. of 15%), stearolic acid (3 g.), and zinc dust (10 g.) contained in a flask closed by a tube bearing a Bunsen valve. After 2 hours, zinc dust (5 g.) and acetic acid (20 c.c.) were added and the process was completed by boiling for 2 hours. The product was mixed with ether, the separated ethereal solution well washed with water, and the acid contained converted into its barium salt (3·5 g.), which was twice crystallised from a mixture of benzene (8 vols.), ethyl alcohol (1 vol.), and a trace of water. The free oleic acid obtained from the barium salt and hot dilute hydrochloric acid was dried in light petroleum (b. p. 40—45°) with anhydrous sodium sulphate, and the solvent removed. The residue, consisting of the pure acid, crystallised on cooling as a glassy mass which froze at 12·5° in one experiment and at 13° in another. These freezing points were taken with the thermometer immersed in the liquid, and the specimen freezing at 13° froze at the same temperature when mixed with a specimen of pure oleic acid prepared from olive oil, for which we are indebted to Professor A. Lapworth. The characteristic dimorphism exhibited by oleic acid has been described by Kirchner (*Z. physikal. Chem.*, 1913, **79**, 789), and when the acid freezing at 13° was maintained at about 12°, the nuclei of the new modification gradually formed and closely resembled in appearance under the lens the photographs reproduced in the memoir quoted above. The transformed material melted just above 16°. When the acid, dissolved in 300 times its weight of water and one-third of its weight of potassium hydroxide, was oxidised at 0° by the gradual addition of 0·5*N*-potassium permanganate, dihydroxystearic acid was produced in almost theoretical amount; it was best isolated by filtration after the passage of sulphur dioxide. The substance, crystallised from alcohol–benzene, melted at 132°, alone or mixed with a specimen prepared from oleic acid from olive oil. The melting point 136° given in the literature for this acid is too high.

9-*Carbethoxynonanilide.*—Ethyl hydrogen sebacate (22 g.) (Grün

and Wirth, *Ber.*, 1922, **55**, 2207) was heated on the steam-bath for 3 hours with thionyl chloride * (66 g.), the thionyl chloride removed completely by distillation under reduced pressure and exposure of the residue to a vacuum, and 9-carbethoxynonoyl chloride, thus obtained in good yield, treated with an excess of aniline. The *anilide* crystallised from light petroleum containing a little benzene in colourless needles, m. p. 63° (Found: C = 70·9; H = 8·7. $C_{18}H_{27}O_3N$ requires C = 70·8; H = 8·8%).

10-*Ketostearic Acid.*—The condensation of ethyl sodio-*n*-heptylmalonate with 9-carbethoxynonoyl chloride was carried out like that in the case of the related derivative of acetoacetic acid. The product was an oil which on hydrolysis by alkali gave heptylmalonic and sebacic acids, but no ketostearic acid. Dilute sulphuric acid gave a similar result, but 1% aqueous oxalic acid caused partial hydrolysis in the desired direction and a very small yield of 10-ketostearic acid, m. p. 77°, could be isolated after boiling during a week. The process was obviously unsatisfactory and was abandoned in favour of the following method.

Sodium (1·2 g.) was granulated under toluene, washed with ether, suspended in ether (75 c.c.), and a solution of ethyl 2-acetylnonoate (11·5 g.) (Jourdan, *Annalen*, 1879, **200**, 105) in ether (75 c.c.) gradually added. The clear solution of the sodio-derivative obtained by gentle heating was cooled in melting ice and treated with 9-carbethoxynonoyl chloride (12·5 g.) in ether (20 c.c.). After 1 hour, the mixture was boiled for 10 minutes, cooled, washed with water, and the ether evaporated. The residue was shaken with 5% aqueous sodium hydroxide (200 c.c.) for 2 days and then, after acidification with acetic acid, collected again by means of ether, boiled during 24 hours with 5% sulphuric acid (300 c.c.), and the mixture steam-distilled; the oil in the distillate was methyl *n*-octyl ketone (Jourdan, *loc. cit.*). The residue in the flask was once more collected by means of ether and boiled during 1·5 hours with 5% aqueous sodium hydroxide (100 c.c.). On cooling, the gelatinous precipitate first formed rapidly changed to colourless leaflets, m. p. 212°. The acid obtained from this salt crystallised from alcohol and from light petroleum in colourless plates, m. p. 83°, and at the same temperature when mixed with 10-ketostearic acid derived from stearolic acid as described below. The two specimens were carefully compared and no differences could be discerned. Stearolic acid was dissolved in concentrated sulphuric acid (5 parts) as recommended by Baruch (*Ber.*, 1884, **27**, 174), but water was not added after 12 hours, the solution being filtered by glass wool

* Purified by distillation after boiling under reflux with 1% of aluminium chloride and 1% of sulphur.

and kept in an open vessel. The crust which formed at the surface was removed from time to time, drained on porous porcelain, crystallised from alcohol, converted into sodium salt, which was also crystallised from alcohol, finally the recovered acid was crystallised twice from light petroleum and twice from benzene. The product melted at 83°, whereas the crude acid melts at about 72° and the highest recorded melting point is 76°. 10-*Hydroxystearic acid*, prepared in theoretical yield by the reduction of pure sodium 10-ketostearate in dry alcohol by means of sodium, melts at 84·5°. This acid yields 10-iodostearic acid by the action of phosphorus tri-iodide and water, and Arnaud and Posternak (*Compt. rend.*, 1910, **150**, 1525) have carefully examined the products of the action of alcoholic potassium hydroxide on this iodostearic acid, a reaction first investigated by Saytzeff (*J. pr. Chem.*, 1887, [ii], **35**, 387). The former authors showed that oleic acid, hydroxystearic acid, and isomeric elaidic acids can be isolated.

Ethyl 2-*Acetyl*-n-*tridecoate*, $CH_3{\cdot}[CH_2]_{10}{\cdot}CHAc{\cdot}CO_2Et$.—12·2 Grams of an oil, b. p. 185°/17 mm., were obtained according to the usual method employing sodium (1·4 g.), alcohol (17·5 g.), ethyl acetoacetate (11·8 g.), *n*-undecyl iodide (17 g.); the time of reaction was 3·5 hours (Found: C = 72·1; H = 11·1. $C_{17}H_{32}O_3$ requires C = 71·8; H = 11·3%).

6-*Ketostearic Acid* (*Lactarinic Acid*).—Ethyl hydrogen adipate, prepared by a method analogous to that employed by Grün and Wirth (*loc. cit.*) in the semi-hydrolysis of diethyl sebacate, was converted into the acid chloride by means of pure thionyl chloride. 5-Carbethoxyvaleryl chloride (8·5 g.) dissolved in ether (10 c.c.) was added to a solution of ethyl sodio-2-acetyl-*n*-tridecoate (13·5 g.) in ether (75 c.c.) at 0°; after remaining ½ hour at room temperature, the mixture was boiled under reflux for 15 minutes. The washed and isolated product was shaken for 16 hours with 5% aqueous sodium hydroxide (300 c.c.), collected as in the previous example, and boiled with 5% sulphuric acid (600 c.c.) for 24 hours. Steam distillation separated some methyl *n*-dodecyl ketone, m. p. 33—34° (Krafft, *Ber.*, 1882, **15**, 1708), and the residue in the flask was collected and heated for 4·5 hours with boiling 5% aqueous sodium hydroxide (200 c.c.). The sodium salt (4·2 g.) which crystallised on cooling was collected, and the acid isolated and crystallised from alcohol. The colourless plates melted at 87°, alone or mixed with an authentic specimen of lactarinic acid (Found: C = 72·7; H = 11·3. Calc. for $C_{18}H_{34}O_3$, C = 72·5; H = 11·4%).

The *oxime*, m. p. 59—61°, crystallised from light petroleum in microscopic needles and was transformed by concentrated sulphuric acid at 100° into an amide crystallising from alcohol in colourless

needles, m. p. 104°. These m. pt's. agree with those given by Bougault and Charaux (*loc. cit.*).

3-*Carbomethoxypropionanilide*, $CO_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NHPh$.—Methyl hydrogen succinate, being a solid, m. p. 58°, was used in preference to the corresponding ethyl derivative in the synthesis of 4-ketopalmitic acid. Succinic anhydride, conveniently obtained by the action of thionyl chloride on the acid, was converted into the semi-ester by the method of Bone, Sprankling, and Sudborough (J., 1904, **85**, 530). 3-*Carbomethoxypropionyl chloride*, derived from the acid by the action of thionyl chloride, is a colourless liquid, b. p. 93°/18 mm., and reacts with aniline with formation of 3-carbomethoxypropionanilide, which crystallises from light petroleum–benzene, as also from ether, in colourless needles, m. p. 97—99° (Found: C = 63·8; H = 6·4. Calc. for $C_{11}H_{13}O_3N$, C = 63·7; H = 6·3%). The same substance has been prepared by the action of methyl alcohol and hydrogen chloride on succinanil (van der Meulen, *Rec. trav. chim.*, 1896, **15**, 341; Hoogewerth and van Dorp, *ibid.*, 1898, **17**, 200).

4-*Ketopalmitic Acid.*—A solution of 3-carbomethoxypropionyl chloride (6 g.) in ether (30 c.c.) was added to the sodio-derivative from ethyl 2-acetyl-*n*-tridecoate (11 g.) and granulated sodium (0·9 g.) in ether (320 c.c.). The mixture was cooled in ice-water, kept over-night, and boiled under reflux for ½ hour. The washed and isolated product was hydrolysed by shaking for 6 hours with 5% potassium hydroxide (300 c.c.), boiling for 30 hours with 5% sulphuric acid (250 c.c.) and for 3 hours with 5% potassium hydroxide. The potassium salt did not separate on cooling and, on acidification of the solution, 5·1 g. of almost pure 4-ketopalmitic acid were obtained. The substance crystallises from light petroleum in colourless clusters of waxy, lanceolate plates, m. p. 91—92° (Found: C = 71·3; H = 11·0. $C_{16}H_{30}O_3$ requires C = 71·1; H = 11·1%). The *oxime* is readily soluble in most organic solvents and crystallises from light petroleum in colourless needles, m. p. 54°.

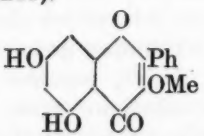
We desire to express our thanks to the Food Investigation Board for grants which have enabled one of us to take part in this investigation.

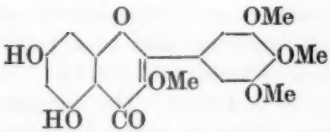
THE UNIVERSITY, MANCHESTER. [*Received, November 10th*, 1924.]

XXVIII.—*A Synthesis of Myricetin and of a Galangin Monomethyl Ether Occurring in Galanga Root.*

By Jan Kalff and Robert Robinson.

Allan and Robinson (J., 1924, **125**, 2192) have described an extremely simple method of preparation of 7-hydroxy-3-methoxyflavone by hydrolysis of the product of the action of benzoic anhydride and sodium benzoate on ω-methoxyresacetophenone at 180—185°. On applying the reaction to ω-methoxyphloracetophenone (Slater and Stephen, J., 1920, **117**, 316), we have now obtained an excellent yield of 5 : 7-dihydroxy-3-methoxyflavone (I), which is identical with the galangin monomethyl ether isolated from galanga root, the rhizome of *Alpinia officinarum* (Hance), by Testoni (*Gazzetta*, 1900, **30**, ii, 327). The formation of phloroglucinol and benzoic acid by the aërial oxidation of an alkaline solution of the substance was observed by A. G. Perkin and Allison (J., 1902, **81**, 472) and led to the suggestion that it is galangin 3-monomethyl ether. This conclusion is now confirmed by synthesis, and the occurrence of the methyl group in this position in the molecule of a naturally occurring flavonol is of interest because there is reason to believe that certain of the anthocyanidins are similarly constituted in respect of this structural detail. The attractive view that the anthocyanin and anthoxanthin pigments are intimately and genetically related derives support from the accumulation of such coincidences. Galangin itself is obtained by demethylation of the methyl ether, and this flavonol has been previously synthesised by v. Kostanecki and Tambor (*Ber.*, 1899, **32**, 2260).

(I.) 



(II.)

Myricetin was first isolated by A. G. Perkin and Hummel (J., 1896, **69**, 1287) from the bark of *Myrica nagi* (Thunb), and as a result of this and subsequent investigations (Perkin, J., 1902, **81**, 204; 1911, **99**, 1721; Perkin and Phipps, J., 1904, **85**, 62) has been regarded as 3 : 5 : 7 : 3′ : 4′ : 5′ :-hexahydroxyflavone (II with H in place of Me). Myricetin is somewhat widely distributed in nature, and it is the flavonol which should yield a delphinidin salt on reduction in acid solution. The synthesis of the colouring matter is a further example of the new and convenient method of preparation of the flavonols. ω-Methoxyphloroacetophenone was heated

with trimethylgallic anhydride and sodium trimethylgallate, and the product hydrolysed. The 5 : 7-dihydroxy-3 : 3′ : 4′ : 5′-tetramethoxyflavone (II) thus obtained yields myricetin on demethylation. Phloroglucinol is converted in this manner into myricetin through two isolated intermediate stages only, and the synthesis is also available as a preparative method.

EXPERIMENTAL.

Galangin 3-Monomethyl Ether (I).—A mixture of ω-methoxyphloroacetophenone (5 g.), sodium benzoate (6 g.), and benzoic anhydride (15 g.) was heated (oil-bath at 180°) during 8 hours, after which alcohol (75 c.c.) was added to the dark red, semi-solid mass, and potassium hydroxide (8·5 g.) in water (10 c.c.) gradually introduced to the boiling solution. After refluxing for ½ hour, the greater part of the alcohol was evaporated, the residue dissolved in water, and the flavonol precipitated as a brown powder by saturating the liquid with carbon dioxide, collected, washed, and dried (6·5 g.). The substance was purified through its *diacetyl* derivative, prepared by the action of boiling acetic anhydride during 2 hours. After two crystallisations from alcohol (charcoal), the substance was obtained in long, very pale yellow needles, m. p. 175—176° (Found: C = 65·3; H = 4·4. $C_{20}H_{16}O_7$ requires C = 65·2; H = 4·4 %). Testoni (*Gazzetta*, 1900, **30**, ii, 327) states that the diacetate derived from the galangin monomethyl ether from galanga root melts at 175—176°. The diacetylgalangin methyl ether was hydrolysed by means of an excess of 10% aqueous potassium hydroxide on the steam-bath. The phenol precipitated by hydrochloric acid may be crystallised from alcohol, acetic acid, or ethyl acetate in rectangular, yellow plates, m. p. 299°, soluble in dilute aqueous potassium hydroxide to an intense yellow solution (sodium salt, yellow needles) and in sulphuric acid to a yellow solution exhibiting green fluorescence (Found: C = 67·2; H = 4·4. $C_{16}H_{12}O_5$ requires C = 67·6; H = 4·3%). The properties of this substance agree with those ascribed to natural galangin monomethyl ether by Testoni (*loc. cit.*) and the identity was proved by the fact that the melting point of the synthetical material was not lowered by admixture with the natural product, for a specimen of which we are greatly indebted to Professor A. G. Perkin. Demethylation by means of boiling hydriodic acid (*d* 1·7), mixed with a quarter of its weight of acetic anhydride, during 40 minutes resulted in the formation of galangin, m. p. 214—215°, after crystallisation from alcohol.

Myricetin 3 : 3′ : 4′ : 5′-Tetramethyl Ether (II).—Pyridine (52 g.) was gradually added to a solution of trimethylgalloyl chloride (35 g.) (Perkin and Weizmann, J., 1906, **89**, 1655) in ether (250 c.c.)

and, after 2 hours, ice and then water was gradually introduced, and the trimethyl gallic anhydride, which is sparingly soluble in ether, collected, washed with dilute aqueous sodium carbonate solution, and dried (yield 75%). This product melted at 159° (corr.) and was employed without further purification (Fischer and Freudenberg, *Ber.*, 1913, **46**, 1129, give 160—161° [corr.] as the m. p. of the pure substance). A mixture of trimethylgallic anhydride (23 g.), sodium trimethylgallate (10 g.), and ω-methoxyphloroacetophenone (4·5 g.) was heated at 175° for 3 hours. The mixture was at first completely fluid, but as the reaction proceeded it became a dark red paste. As in the previous example, the flavonol was isolated by treatment of the crude product with an alcoholic solution of potassium hydroxide (8 g.) and precipitation of the phenolic material by means of carbon dioxide after removal of the alcohol and solution of the residue in water.

The crude material (8·2 g.) was acetylated by boiling with an excess of acetic anhydride, and the derivative crystallised from alcohol. 3 : 3′ : 4′ : 5′-*Tetramethylmyricetin diacetate* was obtained in long, pale yellow needles, m. p. 159° (corr.) (Found : C = 60·3; H = 4·9. $C_{23}H_{22}O_{10}$ requires C = 60·2; H = 4·9%). On hydrolysis by means of boiling concentrated hydrochloric acid, this derivative yields myricetin tetramethyl ether, which crystallises from alcohol in thin, glistening, pale yellow plates, m. p. 276—277·5° (Found : C = 60·6; H = 4·8. $C_{19}H_{18}O_8$ requires C = 60·9; H = 4·8%). This sparingly soluble substance is almost devoid of mordant dyeing properties.

Myricetin.—The tetramethyl ether was demethylated by treatment for 2 hours with a boiling mixture of colourless hydriodic acid (*d* 1·7) (4 parts) and acetic anhydride (1 part). The red, crystalline myricetin hydriodide was collected, decomposed by hot water, and the yellow precipitate isolated. The substance crystallised from aqueous alcohol in bright yellow needles and showed all the highly characteristic reactions of myricetin as described by Perkin and his collaborators (*loc. cit.*). The remarkable behaviour with alkalis and with mineral acids, the reactions with lead acetate and ferric chloride, and the dyeing properties were examined. The melting point was about 360°, but, as stated by Perkin, the determination is difficult on account of blackening. For this reason, the substance was converted in the usual manner into the hexa-acetate, which crystallised from alcohol in long, silky, colourless needles, m. p. 214—215° * (corr.) (Found : C = 56·8; H = 3·7. Calc. for $C_{27}H_{22}O_{14}$, C = 56·8; H = 3·9%).

* The melting point, 211–212°, given in the literature is presumably uncorrected.

We are greatly indebted to Professor A. G. Perkin for a specimen of myricetin hexa-acetate. The derivative prepared from natural myricetin when mixed with the synthetical material did not depress its melting point. Direct comparison further confirmed the identity of the specimens.

We desire to thank the Ramsay Memorial Fellowship Trust for a Fellowship (Netherlands) which has enabled one of us to take part in this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, November 20th*, 1924].

XXIX.—*Researches on Residual Affinity and Co-ordination. Part XXIII. Interactions of Trimethylstibine and Platinic and Palladous Chlorides.*

By GILBERT T. MORGAN and VICTOR EMMANUEL YARSLEY.

THE lower chlorides of platinum and palladium combine additively with ammonia, pyridine, thioethers, selenoethers and the trialkylphosphines and -arsines to give rise to co-ordination compounds of the general types $PtCl_2,2X$, $PtCl_2,4X$, $PdCl_2,2X$, and $PdCl_2,4X$.

In the case of the amine and pyridine derivatives of platinous chloride, there is considerable foundation for the belief that the compounds $PtCl_2,2X$ exist in *cis-* and *trans-*modifications, the four associating units and the central platinum atom being regarded as being in the same plane. A change of orientation from this coplanar arrangement to a tetrahedral configuration would, however, result in the disappearance of the above-mentioned *cis-* and *trans-*isomerism.

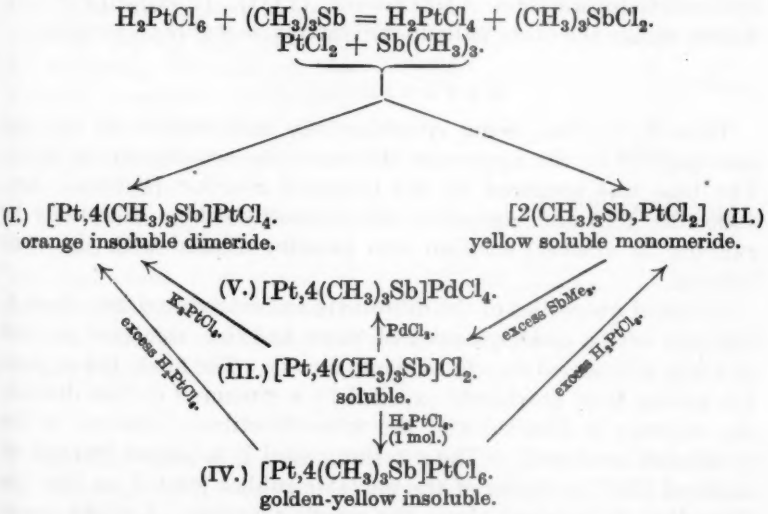
This change may occur with an increase in the atomic volume of the associating units and although coplanar arrangement may be the rule with amines it by no means follows that this configuration will persist in the additive compounds with phosphines and arsines.

The compounds with trimethyl- and triethyl-phosphines were discovered by Cahours and Gal (*Compt. rend.*, 1870, **70**, 897; **71**, 208, 1381), who obtained two products of empirical formula $PtCl_2,2PR_3$, in each case, one white and the other yellow. Transformation of the latter to the former modification was noticed on heating, but no evidence was given, or has since been forthcoming, that the two substances have the same molecular complexity. These authors also obtained two isomeric arsenical derivatives, $PtCl_2,2As(C_2H_5)_3$, both of which were yellow but differed in solubility. But here again there is no evidence as to molecular complexity.

In the experiments described below, chloroplatinic acid and palladous chloride have been treated in turn with trimethylstibine. With the platinic compound reduction occurs giving rise to trimethylstibine dichloride, and the resulting platinous compound then interacts with more trimethylstibine forming one or two additive compounds according as to whether the reaction occurs in aqueous or alcoholic solution. In the former medium, an orange product is formed which is insoluble in water and organic solvents. In alcohol, this orange compound is precipitated, but a soluble substance is also formed which crystallises from organic media in pale yellow leaflets.

Analyses and molecular-weight determinations indicate that the soluble yellow product is *bistrimethylstibinedichloroplatinum* (II). The orange substance is evidently either isomeric or polymeric with this yellow compound, for it passes quantitatively into the latter at 60° or when left for several months at the ordinary temperature.

Owing to the insolubility of the orange compound in all neutral solvents, its molecular complexity cannot be determined by physical methods, but its structure has been ascertained by preparing it in two other ways.



1. With excess of trimethylstibine, the yellow and orange compounds are both converted slowly into the soluble *tetrakistrimethylstibineplatinous chloride* (III), and this salt on treatment with cold aqueous potassium platinochloride gives rise to the orange compound, which is thereby shown to be *tetrakistrimethylstibineplatinous platinochloride* (I). With chloroplatinic acid or palladous

chloride tetrakistrimethylstibineplatinous chloride gives rise respectively to *tetrakistrimethylstibineplatinous platinichloride* (IV) or *tetrakistrimethylstibineplatinous palladochloride* (V).

2. The former of those two salts when hydrolysed with excess of chloroplatinic acid furnishes *bistrimethylstibinedichloroplatinum* (II) and *tetrakistrimethylstibineplatinous platinochloride* (I), in the proportions of 17 : 1.

In the palladium series, trimethylstibine and palladous chloride interact at low temperatures to form an orange additive product, but this changes spontaneously on slight rise of temperature to a yellow substance, *bistrimethylstibinedichloropalladium* (VI). Excess of trimethylstibine converts this to the soluble orange *tetrakistrimethylstibinepalladous chloride* (VII), a soluble salt less stable than

(VI.) $[2(CH_3)_3Sb,PdCl_2]$. $[Pd,4(CH_3)_3Sb]Cl_2$ (VII.)

its platinum analogue, which did not give with palladous chloride an insoluble product corresponding with the orange dimeride of the platinous series.

Digested with dilute hydrochloric acid, the tetrakis compound is converted into a light yellow, crystalline substance, *trimethylstibinedichloropalladium hydrochloride* (VIII), $[(CH_3)_3Sb,PdCl_3]H$, which, unlike the other pallado-derivatives, is stable on keeping.

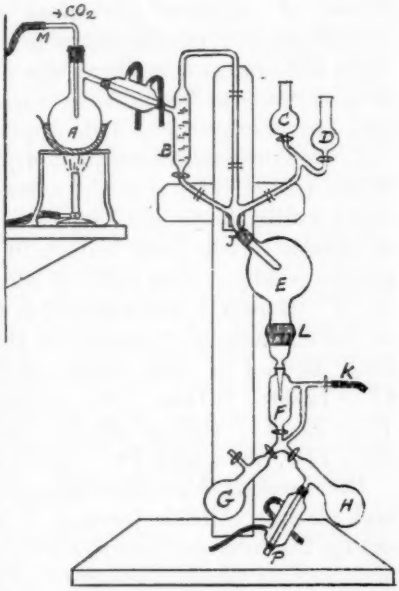
Experimental.

Trimethylstibine, being spontaneously inflammable in air, was manipulated in the apparatus shown in the accompanying figure. The base was prepared by the Grignard reaction (Hibbert, *Ber.*, 1906, **39**, 160) and converted into trimethylstibine dibromide by running its ethereal solution into bromine diluted with the same solvent.

Weighed quantities of the dibromide are introduced into flask A, together with a small quantity of water and the calculated amount of finely granulated zinc (Kahlbaum No. 1). The air in the apparatus having been previously expelled by a stream of carbon dioxide, the mixture is distilled and the trimethylstibine collected in the graduated receiver B. The reaction vessel E is turned through an angle of 120° by means of the movable rubber joint J, so that the filter disk, L, is raised above the reacting liquids. A slight excess of aqueous platinic or palladous chloride solution is delivered into E from the tap funnel, D, and to this is slowly added the calculated amount of trimethylstibine from the graduated receiver B. As the tertiary stibine is not miscible with aqueous solutions, the chemical combination is facilitated by shaking the vessel E and when the reaction is completed the apparatus is rotated so that the

attachments of vessel E are now in the vertical position as shown by the diagram. By aspiration at K, the liquid contents of E are drawn through the filter, L, on which the insoluble product is collected. The precipitate is now washed with ether introduced through the tap funnel, C, and the ethereal washings are aspirated into the receiver F. Here the aqueous and ethereal filtrates are separated, the former being drawn off into the flask G, whilst the latter is collected in distilling flask, H, which is fitted with a condenser, P. On distilling off the solvent, a residue is obtained of the ether-soluble product, which is shown below to be trimethylstibine dichloride.

Fig. 1.



When alcoholic platinic chloride is employed the reaction is more vigorous because of the miscibility of trimethylstibine with this medium. The insoluble product is collected as before on filter L, whilst the alcoholic filtrate and washings are drawn into flask H. On removing the solvent, the residue contains trimethylstibine dichloride and bistrimethylstibinedichloroplatinum (or palladium).

The whole apparatus is so designed that these platinous and palladous derivatives of highly inflammable trimethylstibine can be prepared, collected and desiccated in an inert atmosphere and out of contact with air.

I. *Platinum Series.*

Tetrakistrimethylstibineplatinous Platinochloride (I).—The addition of trimethylstibine to aqueous platinic chloride in the air-free apparatus resulted in the formation of an orange precipitate insoluble in water or in organic media, which was washed successively with water and ether and dried at the ordinary temperature: 0·2200 gave 0·0990 CO_2, 0·0639 H_2O, C = 12·24, H = 3·21; 0·1807 gave 0·0905 AgCl, Cl = 12·39; 0·0819 gave 0·0454 Sb_2S_3, Sb = 39·86; 0·2465 gave 0·0812 Pt, Pt = 32·94. $C_6H_{18}Cl_2Sb_2Pt$ requires C = 12·17, H = 3·01, Cl = 11·9, Sb = 40·2, Pt = 32·72%.

When left for several months, or rapidly on heating at 65°, this substance undergoes depolymerisation to the pale yellow bistrimethylstibinedichloroplatinum. Both modifications are produced when the interaction of trimethylstibine and platinic chloride is effected in alcoholic solution; the orange dimeric compound is precipitated whereas the monomeric substance remains in solution.

Tetrakistrimethylstibineplatinous platinochloride was also obtained by the following methods, which throw light on its molecular complexity.

1. *From tetrakistrimethylstibineplatinous chloride* (III). A slight excess of aqueous potassium platinochloride was added to tetrakistrimethylstibineplatinous chloride, also dissolved in water, when the orange compound was precipitated quantitatively. This preparation was insoluble in organic solvents and changed at 60° into bistrimethylstibinedichloroplatinum.

2. *From tetrakistrimethylstibineplatinous platinichloride* (p. 189). When treated with a slight excess of aqueous chloroplatinic acid, this platinichloride gave a pale yellow deposit not entirely soluble in organic solvents and leaving in each instance a small amount of orange residue. The ratio of soluble to insoluble product was as 17 : 1. Moreover, when heated at 65°, the orange substance changed in the characteristic manner to the yellow soluble form separating from alcohol in pale yellow leaflets: 0·1139 gave 0·0553 AgCl, Cl = 12·00; 0·1133 gave 0·0653 Sb_2S_3, 0·0364 Pt, Sb = 41·1, Pt = 32·29. $C_6H_{18}Cl_2Sb_2Pt$ requires C = 12·17, H = 3·01, Cl = 11·9, Sb = 40·2, Pt = 32·72%.

Bistrimethylstibinedichloroplatinum (II).—When trimethylstibine and platinic chloride interact in alcoholic solution, the preceding orange insoluble compound separates forthwith, leaving in solution *bistrimethylstibinedichloroplatinum* and trimethylstibine dichloride. After distilling off the solvent, the latter product is removed by ether, leaving the co-ordination compound in a state of purity: 0·1362 gave 0·0661 AgCl, Cl = 12·32. Molecular weight in chloroform gave $M = 605$. $C_6H_{18}Cl_2Sb_2Pt$ requires Cl = 11·9%; $M = 600$.

This monomeric compound was also prepared by heating its polymeride at 60° for several hours. The preparation crystallised from alcohol in pale yellow leaflets and did not yield the green salt of Magnus when treated with Reiset's chloride, $[Pt,4NH_3]Cl_2$: 0·1009 gave 0·0450 CO_2, 0·0303 H_2O, C = 12·12, H = 3·29; 0·1054 gave 0·0526 AgCl, Cl = 12·38; 0·1188 gave 0·0663 Sb_2S_3, Sb = 40·12; 0·1165 gave 0·0379 Pt, Pt = 32·54, M (in chloroform) = 634·7. $C_6H_{18}Cl_2Sb_2Pt$ requires C = 12·17, H = 3·01, Cl = 11·9, Sb = 40·2, Pt = 32·72%; $M = 600$.

The by-product soluble in ether was identified as trimethylstibine dichloride by recrystallisation from this solvent, when it separated in colourless, six-sided crystals: 0·1271 gave 0·1664 AgCl, Cl = 30·02. $C_3H_9Cl_2Sb$ requires Cl = 30·03%. This dichloride is also formed on passing chlorine into an alcoholic solution of bistrimethylstibinedichloroplatinum.

When treated in alcoholic solution with hydroxylamine hydrochloride and sodium acetate, bistrimethylstibinedichloroplatinum was completely reduced. With excess of pyridine, the bistrimethylstibine derivative yields well-defined, colourless needles of tetrapyridineplatinous chloride, readily soluble in water or organic solvents. The pyridine was estimated by the method of Harvey and Sparks (*J. Soc. Chem. Ind.*, 1918, **31**, 41T): 0·0495 gave Py = 55·0; 0·0434 gave 0·0215 AgCl, Cl = 12·25. $C_{20}H_{20}N_4PtCl_2$ requires Py = 54·3, Cl = 12·16%.

Tetrakistrimethylstibineplatinous Chloride (III).—An attempt to prepare this compound by adding excess of trimethylstibine to platinous chloride resulted in the formation of the orange polymeride. This product, when treated with more trimethylstibine, dissolved and the solution gave immediately a dark orange-brown precipitate readily soluble in water or organic solvents, separating from the latter in orange-brown crystals. These are somewhat plastic and difficult to purify, and hence the compound was characterised by conversion into its *chloroplatinate*. For this purpose, the calculated amount of chloroplatinic acid in aqueous solution was mixed with the tetrakis compound, when a golden-yellow deposit was obtained: 0·0802 gave 0·247 Pt, Pt = 30·81. $C_{12}H_{36}Cl_6Sb_4Pt_2$ requires Pt = 30·80%.

Tetrakistrimethylstibineplatinous palladochloride (V), prepared by adding aqueous palladous chloride to an alcoholic solution of the tetrakis compound, crystallised from alcohol in brown leaflets which were very unstable, being decomposed completely on exposure to air for 24 hours: 0·0339 gave 0·0210 Sb_2S_3, 0·0056 Pt, 0·0032 Pd; Sb = 43·9, Pt = 17·08, Pd = 9·46. $C_{12}H_{36}Cl_4SbPtPd$ requires Sb = 43·6, Pt = 17·52, Pd = 9·59%.

Bistri-n-butylstibinedichloroplatinum, $[2(C_4H_9)_3Sb{\cdot}PtCl_2]$.—Attempts to prepare the higher homologues of trimethylstibinedichloroplatinum by adding triethylstibine and tri-*n*-butylstibine to aqueous solutions of platinic chloride led to very unstable, ill-defined products, from which crystalline bistrialkylstibinedichloroplatinums could not be isolated in a state of purity. Analysis of the higher homologue showed that the product had undergone extensive decomposition.

II. *Palladium Series.*

Bistrimethylstibinedichloropalladium (VI).—On adding trimethylstibine to an aqueous solution of palladous chloride cooled in a freezing mixture, an orange-yellow deposit separated, the colour of which persisted at the low temperature. As the temperature rose to normal the product became lemon-yellow and retained this colour on drying. The product was soluble in alcohol or chloroform, but insoluble in water or ether. On prolonged warming, it decomposed without melting, liberating metallic palladium: 0·1059 gave 0·0570 CO_2, 0·0352 H_2O, C = 14·60, H = 3·69; 0·0568 gave 0·0256 PdSb, 0·0323 AgCl, Pd = 21·09, Cl = 14·01; M in chloroform = 515. $C_6H_{18}Cl_2Sb_2Pd$ requires C = 14·2, H = 3·58, Pd = 21·0, Cl = 13·95%; M = 508.

Tetrakistrimethylstibinepalladous Chloride (VII).—The more soluble tetrakis compound formed in the preceding preparation separated from the aqueous filtrate in well-defined, golden-orange needles contaminated with trimethylstibine dichloride, the latter being removed by ether. The tetrakis compound was readily soluble in water, but was decomposed by boiling, although it was more stable than the bis compound: 0·0957 gave 0·0595 CO_2, 0·0292 H_2O, C = 17·00, H = 3·42; 0·0616 gave 0·0079 Pd, Pd = 12·80. $C_{12}H_{36}Cl_2Sb_4Pd$ requires C = 17·05, H = 4·28, Pd = 12·6%.

This tetrakis compound was also obtained by the action of excess of trimethylstibine on bistrimethylstibinedichloropalladium, although the yield was diminished by reduction of a portion of the palladium present in the latter reagent. The stability of the resulting product was increased materially by keeping it in the dark throughout its preparation and separation. When boiled for some time with dilute hydrochloric acid or a large excess of chloroform, this tetrakis derivative was converted into a lemon-yellow substance (VIII) soluble in water or organic media and distinctly acidic to bromophenol-blue. Unlike the other pallado-derivatives (VI and VII), this product was stable on keeping in the air and gave a light brown precipitate with cæsium hydroxide: 0·1121 gave 0·0490 Sb_2S_3 and 0·0321 Pd, Sb = 31·1, Pd = 28·6. $C_3H_{10}Cl_3SbPd$ requires Sb = 32·03, Pd = 28·07%.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research, to the Salters' Institute of Industrial Chemistry, and to Messrs. Brunner Mond and Company, Limited, for grants which have helped to defray the expense of this investigation.

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XXX.—*αγ-Dialdehydopropane-ββ-dicarboxylic Acid and αγ-Dialdehydopropane-β-carboxylic Acid.*

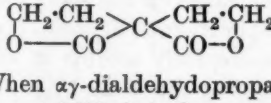
By WILLIAM HENRY PERKIN, jun., and HERBERT SHEPPARD PINK.

THIS communication is a continuation of the work of Perkin and Sprankling (J., 1899, **75**, 11), who showed that ethyl acetalmalonate, obtained when ethyl sodiomalonate is heated with bromoacetal, yields, on hydrolysis, acetalmalonic acid and that this acid, when heated with water at 180°, loses carbon dioxide with the formation of β-aldehydopropionic acid :

$$(EtO)_2CH\cdot CH_2\cdot CH(CO_2Et)_2 \longrightarrow (EtO)_2CH\cdot CH_2\cdot CH(CO_2H)_2 \longrightarrow CHO\cdot CH_2\cdot CH_2\cdot CO_2H.$$

The oxidation of the latter acid to succinic acid, its reduction to butyrolactone, and its conversion into terephthalic acid by treatment with alkali were described. It is now shown that the potassium derivative of ethyl acetalmalonate reacts with bromoacetal with the formation of ethyl diacetalmalonate (A) and that this ester, on hydrolysis with baryta, yields diacetalmalonic acid, $(EtO)_2CH\cdot CH_2\cdot C(CO_2H)_2\cdot CH_2\cdot CH(OEt)_2$.

When the ester (A) is left in contact with *N*-hydrochloric acid in the cold, it is converted into the *ester* of *αγ-dialdehydopropane-ββ-dicarboxylic acid*, $CHO\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CHO$, but if concentrated hydrochloric acid is employed, further hydrolysis takes place and *αγ-dialdehydopropane-ββ-dicarboxylic acid* is produced. Apart from the method of synthesis, the constitution of this acid is demonstrated by the facts that it is converted on reduction into bis-γ-butyrolactone-αα-spiran (I) which Leuchs and Gieseler (*Ber.*, 1912, **44**, 2114) obtained by the action of ethylene bromoacetate on ethyl sodiomalonate and that, on oxidation, it yields propane-αββγ-tetracarboxylic acid (II), which, at its melting point, is decomposed with elimination of carbon dioxide and formation of tricarballylic acid (compare Bischoff, *Ber.*, 1896, **29**, 267).

(I.)  $CO_2H\cdot CH_2\cdot C(CO_2H)_2\cdot CH_2\cdot CO_2H$ (II.)

When αγ-dialdehydopropane-ββ-dicarboxylic acid is heated with water at 180°, it is decomposed with elimination of carbon dioxide and formation of *αγ-dialdehydopropane-β-carboxylic acid*,

$$CHO\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CHO.$$

EXPERIMENTAL.

Ethyl Diacetalmalonate.—The ethyl acetalmalonate required for the preparation of this substance was obtained by adding ethyl

malonate (100 g.) and bromoacetal (80 g.) to sodium (14·2 g.) dissolved in alcohol (200 c.c.). The mixture was heated in an autoclave fitted with a mechanical stirrer for 4 hours, the temperature of the surrounding oil-bath being kept at 180°. The product was worked up as described in the previous communication (J., 1899, **75**, 13), and the ester (72 g.) distilled at 163—165°/20 mm. In the preparation of the diacetal derivative, potassium (8 g.) is melted under boiling toluene (50 c.c.), pulverised by shaking, cooled, and ethyl acetalmalonate (55 g.) added very gradually. A vigorous action takes place and if the ester is added too rapidly, the heat generated is sufficient to raise the toluene to the boiling point and the solution turns brown. When all the ethyl acetalmalonate has been introduced and the last traces of metal have disappeared, bromoacetal (40 g.) is added and four such portions are united and heated in the autoclave during 6 hours with constant stirring, the temperature of the oil-bath being maintained at 200°. After standing overnight, the product is transferred to flasks, the toluene removed under reduced pressure, the residue mixed with water and ether, the ethereal extract well washed, dried over anhydrous potassium carbonate, and the ether distilled off. The distillation is continued under reduced pressure, when unchanged ethyl acetalmalonate (80 g.) comes over at 140—170°/20 mm.; the thermometer then rises rapidly to 187°, between which temperature and 200° the main portion of the ethyl diacetalmalonate passes over; there is a further fraction at 200—250° which has not been examined. On redistillation, *ethyl diacetalmalonate* is obtained as a colourless, rather viscid oil, b. p. 192—196°/18 mm., $d_{22}^{22°}$ 1·031 (Found: C = 58·3; H = 9·2. $C_{19}H_{26}O_8$ requires C = 58·2; H = 9·2%).

Hydrolysis.—(i) By Alkali. The ester (5 g.) was mixed with a methyl-alcoholic solution of barium hydroxide (32 c.c. of a solution of 16 g. of $Ba(OH)_2,8H_2O$ in 100 c.c. of methyl alcohol = 25% excess) and boiled on the steam-bath for 4 hours. Water (10 vols.) was then added, the whole saturated with carbon dioxide, and the filtrate from the barium carbonate concentrated on the steam-bath, but the salt did not crystallise. On evaporation to dryness, a pale yellow, brittle salt remained which is moderately soluble in water (Found: Ba = 31·0. $C_{15}H_{26}O_8Ba$ requires Ba = 29·1%). The powdered barium salt (5 g.) was mixed with a little water, and slightly less than the calculated quantity (21 c.c.) of *N*-sulphuric acid added with vigorous stirring. After standing over-night, the whole was filtered, the filtrate extracted repeatedly with pure ether, the ethereal solution dried over anhydrous magnesium sulphate, and the ether allowed to evaporate, when *diacetalmalonic acid* was left as a pale, viscid syrup which showed no tendency to crystallise.

After remaining for 3 days in a vacuum desiccator over solid potassium hydroxide, this was analysed (Found: C = 53·3; H = 8·3. $C_{15}H_{28}O_8$ requires C = 53·6; H = 8·3%. On titration with *N*/10-alcoholic potassium hydroxide, 0·22 neutralised 0·0533 KOH, whereas this amount of a dibasic acid, $C_{15}H_{28}O_8$, should neutralise 0·0524 KOH).

(ii). By Concentrated Hydrochloric Acid. Ethyl diacetalmalonate (10 g.) was well shaken with concentrated hydrochloric acid (30 c.c.), when complete solution took place, and, after 24 hours, the rather dark liquid was diluted with water, filtered from a little tarry matter, and evaporated to a small bulk under reduced pressure, the temperature not being allowed to rise above 30°. After further evaporation over sulphuric acid in a vacuum desiccator, a pale brown syrup resulted and this was mixed with water and again evaporated, the operation being repeated several times. The syrup remained as such for 7 weeks and then suddenly crystallised and the mass was drained on porous porcelain and crystallised from water, from which it separated in colourless prisms (Found: C = 44·7; H = 4·5. $C_7H_8O_6$ requires C = 44·7; H = 4·3%). *αγ-Dialdehydopropane-ββ-dicarboxylic acid* melts at 122° with decomposition and is readily soluble in water, alcohol, or acetone, sparingly so in ether, and almost insoluble in petroleum, benzene, chloroform, or carbon tetrachloride. On titration, 0·1562 neutralised 0·0665 NaOH, whereas this amount of a dibasic acid, $C_7H_8O_6$, should neutralise 0·0664 NaOH. A neutral solution of the ammonium salt gives, with silver nitrate, a white precipitate which rapidly darkens and silver is deposited.

The *di*-p-*nitrophenylhydrazone* separated as a yellow, crystalline precipitate when the aqueous solution of the acid (0·6 g.) was mixed with *p*-nitrophenylhydrazine (0·85 g.), dissolved in dilute acetic acid, and separated from alcohol in glistening plates, m. p. 156° (decomp.) (Found: N = 18·2. $C_{19}H_{18}O_8N_6$ requires N = 18·3%). The *ethyl* ester was obtained when ethyl diacetalmalonate (15 g.) was well shaken with *N*-hydrochloric acid (30 c.c.) and, after remaining for 24 hours, the whole was several times extracted with ether, the extract washed with sodium carbonate, dried over potassium carbonate, and distilled, when the ester passed over at 174—178°/18 mm. The p-*nitrophenylhydrazone*, prepared in dilute acetic acid solution, crystallised from alcohol as a microcrystalline powder, m. p. 170° (Found: N = 16·2. $C_{23}H_{26}O_8N_6$ requires N = 16·3%).

Reduction of αγ-Dialdehydopropane-ββ-dicarboxylic Acid.—The dibasic acid (4 g.), dissolved in water (75 c.c.), was mixed with sodium bicarbonate (15 g.) and treated with sodium amalgam (150 g. of 4%) in a flask fitted with a mechanical stirrer and cooled in ice, the

reduction being complete in about 8 hours. The alkaline solution was acidified with dilute sulphuric acid (10 g.) in water (20 c.c.), concentrated on the steam-bath, repeatedly extracted with chloroform, the extract dried over anhydrous magnesium sulphate, and the chloroform allowed to evaporate. The colourless, crystalline residue separated from water in plates, m. p. 109—110°, and was evidently identical with bis-γ-butyrolactone-αα-spiran described by Leuchs and Gieseler (*loc. cit.*).

Oxidation of αγ-Dialdehydopropane-ββ-dicarboxylic Acid.—The acid (5 g.), dissolved in water (20 c.c.), was mixed with potassium dichromate (5·2 g.) in sulphuric acid (6·9 g.) and water (75 c.c.) and allowed to stand for 12 hours, during which the colour changed to green. The product, evaporated on the steam-bath to 50 c.c., was extracted with ether, the extract dried over anhydrous magnesium sulphate, and the ether allowed to evaporate over sulphuric acid. The oily residue remained for weeks without crystallising, but did so rapidly when a crystal of propane-αββγ-tetracarboxylic acid was introduced. After contact with porous porcelain, the substance separated from ether in needles, melted at 151° with decomposition into carbon dioxide and tricarballylic acid, and was thus identified with propane-αββγ-tetracarboxylic acid.

αγ-Dialdehydopropane-β-carboxylic Acid.—This acid was obtained when αγ-dialdehydopropane-ββ-dicarboxylic acid (4 g.), dissolved in water (16 c.c.), was heated in a sealed tube at 180° for 4 hours. On opening the tube, carbon dioxide escaped and the solution, evaporated in a vacuum over sulphuric acid, deposited a syrup which, even on long standing, did not crystallise (Found : C = 49·5; H = 5·5. $C_6H_8O_4$ requires C = 50·0; H = 5·5%). The *di-p-nitrophenylhydrazone*, obtained by adding a solution of *p*-nitrophenylhydrazine in dilute acetic acid to the aqueous solution of the acid and heating for an hour on the steam-bath, is a yellow, amorphous powder sparingly soluble in the usual solvents. The substance could not be recrystallised and was purified by extraction with hot alcohol and then with ether, when the residue melted at about 198° (decomp.) (Found : N = 20·3. $C_{18}H_{18}O_6N_6$ requires N = 21·3%).

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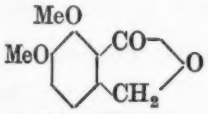
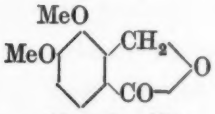
XXXI.—*New Synthesis of the Meconines.*

By George Alfred Edwards, William Henry Perkin, jun., and Francis Wilbert Stoyle.

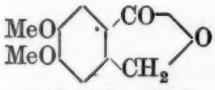
This communication is concerned with a new and direct method for the synthesis of meconine (I) and *m*-meconine (III), and an indirect one for that of ψ-meconine (II), since this substance is quite easily prepared from meconine.



Meconine (I.)



ψ-*Meconine* (II.)



m-*Meconine* (III.)

The direct substitution of the group $-CH_2{\cdot}OH$ into the benzene nucleus has been carried out in a variety of ways. Benzene itself, when treated with *s*-dichlorodimethyl ether in presence of zinc chloride, gives some benzyl chloride (Stephen, Gladding, and Short, J., 1920, **117**, 570), whilst phenols and their ethers condense with formaldehyde in presence of cold aqueous alkali to yield the corresponding benzyl alcohols (Manasse, *Ber.*, 1894, **27**, 2411; Lederer, *J. pr. Chem.*, 1894, [ii], **50**, 225). We have found that the veratric acids do not condense at all readily either with *s*-dichlorodimethyl ether or with cold aqueous formaldehyde, but on boiling with an excess of formaldehyde and concentrated hydrochloric acid the corresponding meconine is formed in moderately good yield according to the scheme

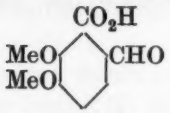
$$(MeO)_2C_6H_3{\cdot}CO_2H + HCHO \longrightarrow (MeO)_2C_6H_2\begin{<}{CO_2H \atop CH_2{\cdot}OH} \longrightarrow$$

$$(MeO)_2C_6H_2\begin{<}{CO- \atop CH_2}{>}O.$$

Meconine, which was originally prepared synthetically in very poor yield by the condensation of *o*-veratric acid with chloral (Fritsch, *Annalen*, 1898, **301**, 51), has now been obtained in 25—30% yields by the above-mentioned method, the formaldehyde unexpectedly substituting entirely in the position ortho to the carboxyl group, as was shown by the identity of the only product isolated with the substance produced by the reduction of opianic acid (IV).

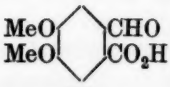
Since meconine on oxidation with manganese dioxide and dilute sulphuric acid is converted into opianic acid (IV), this new synthesis of meconine is also a synthesis of opianic acid, an acid which has not previously been obtained synthetically (compare Perkin and Fargher, J., 1921, **119**, 1724). It further provides a synthesis of

hemipinic acid, since this substance is produced on oxidation with potassium permanganate.



(IV.)

(V.)



(VI.)

An indirect synthesis of ψ-meconine (II) is completed by converting the hemipinic acid, obtained as above, into its anhydride, $(MeO)_2C_6H_2\langle\begin{matrix}CO\\CO\end{matrix}\rangle O$, by dehydration with acetyl chloride, and reducing the product with zinc dust and acetic acid (compare Salomon, *Ber.*, 1887, **20**, 889). Attempts to prepare ψ-opianic acid by oxidation of the ψ-meconine were all unsuccessful, the acid first formed being more easily oxidised than the ψ-meconine itself. Salomon (*loc. cit.*) states that he was unable to bring about this oxidation.

m-Meconine (III), first obtained by Perkin (J., 1916, **109**, 815) from the degradation products of cryptopine derivatives, is similarly produced by the condensation of veratric acid with formaldehyde in presence of concentrated hydrochloric acid, and the synthetic product is in every way identical with the *m*-meconine obtained by Perkin. The lactone ring of this substance is readily opened by alkalis, and on neutralising the cooled solution of the resulting salt with acetic acid, 4 : 5-dimethoxy-2-carboxybenzyl alcohol (V) slowly separates. Strong mineral acids rapidly transform this into the lactone, as does heating it to its melting point or boiling its aqueous solution.

m-Opianic acid (VI), required in the laboratory for synthetic work, is very difficult to obtain, and it was hoped that it might be possible to prepare it from *m*-meconine by oxidation. But although treatment with manganese dioxide and dilute sulphuric acid yielded sufficient *m*-opianic acid for identification, the method in its present form is valueless for the preparation of any quantity of material.

On the other hand, *m*-hemipinic acid in moderately good yield is obtained by the oxidation of *m*-meconine with alkaline permanganate, and this may prove the most convenient method for the preparation of this acid.

Attempts were also made to obtain the methylene ether of 4 : 5-dihydroxyphthalide by the condensation of piperonylic acid with formaldehyde, but even after long boiling, most of the acid was recovered unchanged, only a small yield of an easily oxidisable substance of high molecular weight being produced.

Experimental.

o-Veratric Acid.—The preparation of this acid by the oxidation of *o*-veratraldehyde was best carried out in the following way. The aldehyde (30 g.) was kept boiling under a reflux condenser with water (300 c.c.) and potassium bicarbonate (35 g.) while a hot solution of potassium permanganate (22 g.) in water was added slowly. The cooled and filtered solution, on acidification, yielded *o*-veratric acid, m. p. 120—122°.

Meconine (I).—*o*-Veratric acid (10 g.), formaldehyde solution (25 c.c. of 40%), and concentrated hydrochloric acid (40 c.c.) were boiled together under reflux for 15—20 minutes, when the solution had turned brown and a dark gum had separated. The hot solution was filtered, cooled, and diluted with water, when a mixture of meconine with unchanged acid crystallised out. The solid was washed with sodium carbonate solution to remove the acid, and the meconine (2·5—3 g.) was crystallised from hot water, being obtained in colourless prisms, m. p. 102°. Its identity with the product of the reduction of opianic acid with sodium amalgam was shown by a variety of methods (Found: C = 62·0; H = 5·2. Calc. for $C_{10}H_{10}O_4$, C = 61·6; H = 5·1%).

Opianic Acid (IV).—Meconine (3 g.) was boiled for 3 hours under reflux with dilute sulphuric acid (50 c.c. of 20% solution) and finely powdered manganese dioxide (10 g.). The resulting solution, on cooling and standing, deposited crystals of opianic acid in a practically pure state and in nearly theoretical yield. After a further recrystallisation from hot water, the acid was obtained as colourless prisms, m. p. 146°. It was shown to be identical in every respect with the opianic acid obtained by the oxidation of narcotine with manganese dioxide (Found: C = 57·2; H = 4·9. Calc. for $C_{10}H_{10}O_5$, C = 57·1; H = 4·8%).

Hemipinic Acid.—This acid was best obtained as follows. Opianic acid (10 g.), water (100 c.c.), and lead dioxide (30 g.) were kept at 100° on a water-bath while dilute sulphuric acid was slowly run in. When the evolution of carbon dioxide became rapid, the mixture was cooled, a little more sulphuric acid added, the solution filtered from lead sulphate and excess lead dioxide, and evaporated to small bulk. The hemipinic acid separated on cooling in a hydrated crystalline state, and the anhydrous acid was obtained by heating it at 100° for some time. The amorphous product (7—8 g.) melted at 177°.

Hemipinic anhydride is most conveniently prepared as follows. The acid is heated under reflux with excess of acetyl chloride for 1 hour, when the solution is evaporated to small bulk, and the

anhydride allowed to crystallise from the residue. It is thus obtained as glistening needles, m. p. 168°.

Veratric acid, the preparation of which is not, apparently, described in detail in the literature, is best obtained by slowly adding potassium permanganate (34 g.) in warm water to a constantly stirred mixture of veratraldehyde and water (50 g. in 300 c.c.) kept at 50—60°, a current of carbon dioxide being passed through the solution the whole time. The filtered and cooled solution is extracted with ether to remove any unchanged aldehyde, and the product thrown out by acidification. Veratric acid (50 g.) is thus obtained in a nearly pure, semi-gelatinous state, and without further purification melts at 179°.

m-*Meconine*.—Veratric acid (50 g.) was heated on a water-bath for 12 hours with formaldehyde (55 c.c. of 40% solution) and concentrated hydrochloric acid (200 c.c.). The product was cooled rapidly, diluted with its own bulk of water, and shaken violently until the emulsion formed deposited a gummy substance on the walls of the vessel, leaving a clear solution. The latter, after being filtered and allowed to stand, slowly deposited *m*-meconine (9—15 g.) as a brown, crystalline powder. After washing with sodium carbonate solution, it was recrystallised from dilute alcohol, when it separated as colourless needles, m. p. 155—157°. It was identical with the substance obtained by Perkin (*loc. cit.*) by the reduction of *m*-opianic acid with sodium amalgam.

Further quantities of the lactone were obtained by extracting the resinous substance left clinging to the walls of the reaction vessel with hot caustic soda solution, boiling the filtrate with animal charcoal, and acidifying with hydrochloric acid. The substance which separated on standing recrystallised from aqueous alcohol with a brown colour, but melted at the same temperature as the colourless crystals (Found: C = 61·7; H = 5·0. Calc. for $C_{10}H_{10}O_4$, C = 61·8; H = 5·1%).

4 : 5-*Dimethoxy*-2-*carboxybenzyl Alcohol* (V).—*m*-Meconine was dissolved in the minimum amount of hot caustic soda solution, and the cooled product was just acidified with acetic acid. On standing, the hydroxy-acid separated as clusters of minute needles melting indefinitely at 146—149°. The product is very much more soluble in water than *m*-meconine; but if the solution is kept boiling for a short time *m*-meconine separates as fine needles.

Oxidation of m-*Meconine*.—*m*-Meconine was boiled for 4 hours with manganese dioxide and dilute sulphuric acid in the same proportions as those used in the oxidation of meconine. On filtering and cooling the product, about one-third of the *m*-meconine separated unchanged. The mother-liquor, after being made

alkaline with sodium carbonate, was filtered and the manganese in solution was thus removed as carbonate. The acidified solution was evaporated to dryness in a vacuum, the dry residue extracted with boiling absolute alcohol, and the solution evaporated. The product was taken up in a little boiling water, and one or two drops of phenylhydrazine were added. After the solution had boiled for a short time, the phenylhydrazone of *m*-opianic acid separated as white flocks, and after recrystallisation from alcohol became colourless at 173—176° and melted at 228°. This behaviour was shown by Perkin and Fargher (J., 1921, **119**, 1743) to be characteristic of *m*-opianic acid, and a mixed melting point with some of the phenyl-*m*-opiazone (m. p. 228°) prepared by them established the identity.

m-*Hemipinic Acid.*—A solution of *m*-meconine in a slight excess of aqueous caustic soda was saturated with carbon dioxide, and a little sodium bicarbonate added. The calculated amount of potassium permanganate for the oxidation having been added, the mixture was heated on the water-bath until the colour of the permanganate had been removed, a current of carbon dioxide being passed through the whole time. The filtered and acidified solution was evaporated to small bulk, and the resulting liquid deposited *m*-hemipinic acid as yellow crystals, m. p. 203° (decomp.). This was shown to be identical with the acid obtained by Perkin and Fargher (*loc. cit.*).

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XXXII.—*Method of Measuring the Reduction Potentials of Quinhydrones.*

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IT has been pointed out by one of us (*Trans. Faraday Soc.*, 1923, **19**, 676) that the reduction potential of a quinhydrone can be determined by measuring the potential of an electrode containing, for instance, the *hydroquinone of one quinhydrone* in a solution of the *quinone of another quinhydrone with a known reduction potential*, that is, without preparing the quinhydrone itself or both its con-

stituents. In this paper, the theory of the method is described and some quantitative results are detailed.

Let A, AH_2, and (A,AH_2) be a certain quinone, hydroquinone, and quinhydrone, respectively, and let B, BH_2, and (B,BH_2) be another, similar series. Then, if a solution of the hydroquinone, AH_2, be mixed with a solution of the quinone, B, AH_2 will be partly oxidised to the quinone, A, at the expense of B, which will be partly reduced to its corresponding hydroquinone, BH_2. Starting with equimolecular quantities of AH_2 and B, the reaction may be written

$$aAH_2 + aB \longrightarrow (a-x)AH_2 + xA + (a-x)B + xBH_2 \quad . \quad (1)$$

and the equilibrium set up must be such that the reduction potential π (as measured against a hydrogen electrode) of the mixture $(a-x)AH_2 + xA$ is equal to the reduction potential of the mixture $(a-x)B + xBH_2$.

We have now four electrolytic chains to consider

(*a*) $$Pt\left|\begin{matrix}(a-x)\,.\,mAH_2\\ x\,.\,mA\end{matrix}\right.;\ \text{electrolyte};\ (A,AH_2)\left|\right.Pt$$

with an *E.M.F.* $\phi' = \dfrac{RT}{nF}\log_e\dfrac{x}{a-x} = K\log_{10}\dfrac{x}{a-x}$ . . (2)

(*b*) the similar chain

$$Pt\left|\begin{matrix}x\,.\,mBH_2\\ (a-x)\,.\,mB\end{matrix}\right.;\ \text{electrolyte};\ (B,BH_2)\left|\right.Pt$$

for which

$$\phi = \frac{RT}{nF}\,.\log_e\frac{a-x}{x} = -K\log_{10}\frac{x}{a-x} \quad . \quad . \quad (3)$$

so that $\phi = -\phi'$;

(*c*) the quinhydrone electrode

$$Pt\,|\,(A,AH_2);\ H_2\,|\,Pt$$

with the reduction potential π_0';

and (*d*) the quinhydrone electrode

$$Pt\,|\,(B,BH_2);\ H_2\,|\,Pt$$

with the reduction potential π_0.

Now, for equilibrium we must have

$$\pi = \pi_0' - \phi = \pi_0 + \phi$$

i.e., $$\pi_0' = 2\pi - \pi_0 = 2\phi + \pi_0 \quad . \quad . \quad . \quad . \quad (4)$$

where π is the voltage both of the chain

$$Pt\left|\begin{matrix}(a-x)\,.\,mAH_2\\ x\,.\,mA\end{matrix}\right.;\ H_2\left|\right.Pt$$

and of the chain

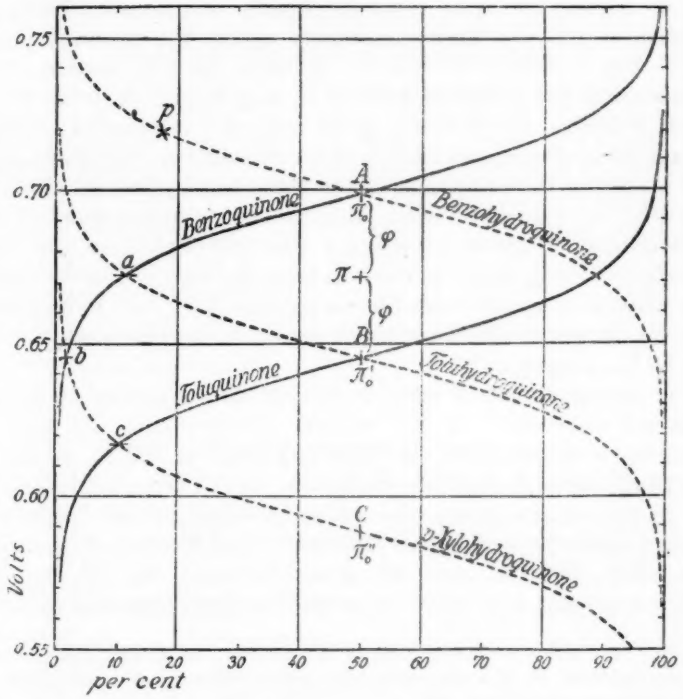
$$Pt\left|\begin{matrix}(a-x)\,.\,mB\\ x\,.\,mBH_2\end{matrix}\right.;\ H_2\left|\right.Pt$$

That is to say, the reduction potential, π_0', of the quinhydrone (A,AH_2) can be determined by measuring

(i) the potential, π, of a mixture of the hydroquinone AH_2 with an equimolecular quantity of the quinone B (or conversely) to a hydrogen electrode.

or (ii) the potential, ϕ, of this mixture to the quinhydrone electrode (B,BH_2).

FIG. 1.



In both cases, we require to know the reduction potential, π_0, of the quinhydrone (B,BH_2) electrode; and obviously the electrolyte, the temperature, and the hydrogen pressure (1 atm.) must be the same in all the electrodes.

Combining equations (3) and (4), we get

$$\pi_0' - \pi_0 = 2\phi = 2K \log_{10}\{x/(a-x)\} =$$
$$(\text{at } 25°)\ 0{\cdot}0591 \log_{10}\{x/(a-x)\},$$

from which equation x may be calculated when π_0 and π_0' have been determined.

Taking the reduction potentials at 25° for benzoquinhydrone, toluquinhydrone, and *p*-xyloquinhydrone as 0·6990, 0·6454, and

0·5886 volt, respectively, the following values for the percentage of quinhydrone unchanged in equimolecular mixtures with quinones are obtained:

Mixture.	% Hydroquinone unchanged.
Benzoquinone + Toluhydroquinone	12·4
Benzoquinone + *p*-Xylohydroquinone	1·4
Toluquinone + *p*-Xylohydroquinone	9·1

Two sources of error must be briefly mentioned. First, the position of the equilibrium markedly affects the accuracy attainable. Fig. 1 shows the relation between the composition of the solution and the potential referred to a hydrogen electrode at 25°. Thus, p denotes the potential (0·72 volt) of a mixture of 18·5% of benzohydroquinone and 81·5% of benzoquinone. Similarly A, B, and C denote the potentials of the three quinhydrones. Now the potential of the equilibrium mixture of toluhydroquinone and benzoquinone is given by point a (the intersection of the corresponding curves), and it is obvious from the figure that the farther this point is removed from the centre line ABC, the more rapidly will the potential change with composition, and the less accurate will be the results.

The second source of error is due to the inequality of the dissociation constants * of the various quinhydrones. At 25°, the dissociation constant of benzoquinhydrone is 0·224, whilst for toluquinhydrone it is 0·095 (Biilmann, *Ann. Chim.*, 1921, [ix], **15**, 151). But by comparing the values obtained by the "mixture" method with those obtained directly by La Mer (*J. Amer. Chem. Soc.*, 1922, **44**, 1954) and one of us (Biilmann, *loc. cit.*) and also in this research, it is seen that satisfactory agreement is obtained,

* Let the initial concentrations of A and BH_2 be a, and the stoicheiometric amounts of the quinones and hydroquinones at equilibrium (as assumed in equation 1) be AH_2, $a - x$; A, x; BH_2, x; and B, $a - x$.

If the concentrations of undissociated quinhydrones AH_2,A and BH_2,B are α and β respectively, the concentrations of the dissociated components will be AH_2, $a - x - \alpha$; A, $x - \alpha$; BH_2, $x - \beta$; and B, $a - x - \beta$.

In the equilibrium set up, the potentials of the mixtures of A and AH_2 and of B and BH_2 against the corresponding two quinhydrones are (equation 2)

$$\phi_A = K \log_{10} \frac{x - \alpha}{a - x - \alpha} \text{ and } \phi_B = K \log_{10} \frac{x - \beta}{a - x - \beta} \text{ respectively.}$$

If, as supposed, $\pi_0' - \pi_0 = 2\phi$, we have $\phi_A = \phi_B$ and, consequently, $(x - \alpha)/(a - x - \alpha) = (x - \beta)/(a - x - \beta)$ or $2x(a - \beta) = a(a - \beta)$.

Consequently, the supposed relation between the potential of the mixture and the reduction potentials of the single quinhydrones is strictly exact if $\alpha = \beta$, *i.e.*, the two quinhydrones have the same dissociation constants [as $k_A = (x - \alpha)(a - x - \alpha)/\alpha$; $k_B = (x - \beta)(a - x - \beta)/\beta$], or if $x = a/2$, *i.e.*, their reduction potentials are identical.

especially when the sparing solubility of the materials dealt with is considered.

In some cases, the equilibrium potential was reached almost instantaneously; in others, it was necessary to wait for some hours before measurement.

Table I records the experimental results.

TABLE I.

Reduction Potentials of Quinhydrones.

Composition of quinhydrone.	π_0 measured in mixture. At 18°.	At 25°.	Other determinations of π_0 at 25°.
$C_6H_3Me(OH)_2,C_6H_3MeO_2$	0·6496	0·6444	0·6454 *
$C_6H_2Me_2(OH)_2,C_6H_2Me_2O_2$	—	0·5893	0·5886
$C_6H_3Cl(OH)_2,C_6H_3ClO_2$	0·7178	0·7124	0·7125 †
$C_6H_3Br(OH)_2,C_6H_3BrO_2$	0·7174	0·7120	0·7151 †
$1:4\text{-}Cl_2:C_6H_2(OH)_2,C_6H_2Cl_2O_2$	0·7280	0·7230	—
$1:4\text{-}Br_2:C_6H_2(OH)_2,C_6H_2Br_2O_2$	0·7280	0·7228	—
$1:4\text{-}ClMe:C_6H_2(OH)_2,C_6H_2MeClO_2$	—	0·6542	0·6566
$1:4\text{-}BrMe:C_6H_2(OH)_2,C_6H_2MeBrO_2$	—	0·6564	0·6591
$C_6HMe_2Cl(OH)_2,C_6HMe_2ClO_2$	—	0·5949	0·5918

* Biilmann, *loc. cit.* † La Mer, *loc. cit.*

EXPERIMENTAL.

Toluhydroquinone.—The toluhydroquinone was recrystallised from toluene immediately before the solution was made up. Equal volumes of 0·01*M*-solutions of toluhydroquinone and benzoquinone in 0·1*N*-hydrochloric acid were mixed and the potentials measured against a benzoquinhydrone electrode, blank platinum electrodes being used.

TABLE II.

$$-Pt\left|\begin{matrix}\text{Toluhydroquinone, } 0{\cdot}005M \\ \text{Benzoquinone, } 0{\cdot}005M\end{matrix}\right.; \begin{matrix}HCl \\ 0{\cdot}1N\end{matrix}; \text{Benzoquinhydrone}\left|Pt+\right.$$

Temp.	25·4°.		18°.	
Minutes	30	60	150	180
Volt, I *	0·0273	0·0273	0·0274	0·0274
„ II *	0·0274	0·0274	0·0275	0·0275
	$\pi_{25°} = 0{\cdot}6444.$		$\pi_{18°} = 0{\cdot}6496.$	

* Duplicate electrodes.

p-*Xylohydroquinone.*—The potentials were measured as above, but the electrolyte was 0·1*N*-sulphuric acid saturated with carbon dioxide, and all the operations were carried out in an atmosphere of this gas.

TABLE III.

$-Pt\left|\begin{matrix}\text{Xylohydroquinone, } 0{\cdot}00125M \\ \text{Toluquinone, } 0{\cdot}00125M\end{matrix}\right.; \ H_2SO_4\ 0{\cdot}1N; \ \text{Benzoquinhydrone}\left|Pt+\right.$

25·4°.

Temp.									
Minutes	25	60	105	135	165	195	1200	1290	1460
Volt, I	0·0689	0·0775	0·0802	0·0809	0·0811	0·0813	0·0820	0·0821	0·0821
„ II	0·0702	0·0773	0·0792	0·0803	0·0807	0·0810	0·0822	0·0822	0·0823

$\pi_{25°} = 0{\cdot}5893.$

Solution prepared from equimolecular quantities of *p*-xylohydroquinone and *p*-xyloquinone in 0·1*N*-sulphuric acid with carbon dioxide treatment as before.

TABLE IV.

$-Pt\left|\begin{matrix}p\text{-Xylohydroquinone, } 0{\cdot}00125M \\ p\text{-Xyloquinone, } 0{\cdot}00125M\end{matrix}\right.; \ H_2SO_4\ 0{\cdot}1N; \ \text{Benzoquinhydrone}\left|Pt+\right.$

Temp.	25·6°				18°	
Minutes	5	45	95	145	185	385
Volt, I	0·1101	0·1104	0·1104	0·1104	0·1103	0·1104
„ II	0·1102	0·1105	0·1105	0·1105	0·1105	0·1106
		$\pi_{25°} = 0{\cdot}5886.$			$\pi_{18°} = 0{\cdot}5940.$	

Without the carbon dioxide treatment, constant potentials could not be obtained. The potentials, measured against the benzoquinhydrone electrode, of a similar electrode prepared without the carbon dioxide treatment are recorded in Table V, and it will be seen that the potentials slowly rise until, after 20 hours, they are practically identical with those in Table IV. This may be due to catalytic oxidation of the hydroquinone on the surface of the platinum, the potential reaching the value in Table IV only when the solution in the electrode vessel is thoroughly mixed by diffusion.

TABLE V.

$-Pt\left|\begin{matrix}p\text{-Xylohydroquinone, } 0{\cdot}00125M \\ p\text{-Xyloquinone, } 0{\cdot}00125M\end{matrix}\right.; \ H_2SO_4\ 0{\cdot}1N; \ \text{Benzoquinhydrone}\left|Pt+\right.$

25·4°.

Temp.						
Minutes	15	60	120	150	1120	1270
Volt, I	0·1072	0·1090	0·1099	0·1100	0·1101	0·1101
„ II	0·1070	0·1093	0·1098	0·1099	0·1103	0·1103

$\pi_{25°} = 0{\cdot}5888.$

Monochlorohydroquinone.—Benzoquinone (10 g.) was heated with 100 c.c. of concentrated hydrochloric acid for ¾ hour on the steam-bath (Wöhler, *Annalen*, 1844, **51**, 155), the solution cooled, diluted with water, and extracted with ether. The residue after evaporation of the ether had m. p. 103° when crystallised twice from chloroform, and 105—105·5° (constant) when crystallised

subsequently from carbon tetrachloride. Levy and Schultz quote 106° (*ibid.*, 1881, **210**, 138), and Schultz quotes 103—104° (*Ber.*, 1882, **15**, 654).

TABLE VI.

−Pt | Benzoquinhydrone; HCl 0·1*N*; Monochlorohydroquinone, 0·005*M* / Benzoquinone, 0·005*M* | Pt+

Temp.	25·4°.			18°.		18°.*
Minutes	15	30	60	120	180	
Volt, I	0·0068	0·0068	0·0068	0·0067	0·0067	0·0066
„ II	0·0067	0·0067	0·0067	0·0066	0·0066	0·0066
	$\pi_{25°} = 0·7124.$			$\pi_{18°} = 0·7178.$		

* After dilution with 3 vols. of 0·1*N*-HCl.

Monobromohydroquinone was prepared after Sarauw's method (*Annalen*, 1881, **209**, 105). Bromine (16 g.) in 100 c.c. of ether was added to 11 g. of hydroquinone in 250 c.c. of ether, and the solution allowed to evaporate at laboratory temperature. The residue was extracted with 250 c.c. of toluene at 90—95°, filtered off, and cooled. Yield 10 g., m. p. 109·8°. Recrystallised from 100 c.c. of toluene, 5 g. gave 3·8 g., m. p. 110·5°, unchanged by further recrystallisation. Sarauw quotes m. p. 110—111°.

TABLE VII.

−Pt | Benzoquinhydrone; HCl 0·1*N*; Monobromohydroquinone, 0·05*M* / Benzoquinone, 0·05*M* | Pt+

Temp.	25·4°.			18°.		18°.*	
Minutes	15	30	55	80	125	15	55
Volt, I	0·0068	0·0065	0·0065	0·0065	0·0065	0·0063	$0·0063_5$
„ II	0·0068	0·0065	0·0065	0·0065	0·0065	0·0064	$0·0064_5$
	$\pi_{25°} = 0·7120.$			$\pi_{18°} = 0·7174.$			

* After dilution with 3 vols. of 0·1*N*-HCl.

2 : 5-*Dichlorohydroquinone.*—Prepared by Ling's method (J., 1892, **61**, 558), and twice crystallised from water, the substance had a constant m. p. 169—170°. Ling quotes 172°, and Levy and Schultz (*loc. cit.*) 166°.

TABLE VIII.

−Pt | Benzoquinhydrone; HCl 0·1*N*; Dichlorohydroquinone, 0·0025*M* / Benzoquinone, 0·0025*M* | Pt+

Temp.	25·4°.		18°.		18°.*
Minutes	15	30	90	150	
Volt, I	0·0121	0·0120	0·0118	0·0118	0·0117
„ II	0·0120	0·0120	0·0118	0·0118	0·0117
	$\pi_{25°} = 0·7230.$		$\pi_{18°} = 0·7280.$		

* After dilution with 3 vols. of 0·1*N*-HCl.

2 : 5-*Dibromohydroquinone.*—Prepared by the method of Benedict (*Monatsh.*, 1880, **1**, 345) and of Sarauw (*loc. cit.*), and twice crystal-

lised from water, the compound had the m. p., 186°, recorded by those investigators.

TABLE IX.

−Pt | Benzohydroquinone; HCl 0·1*N*; Dibromohydroquinone, 0·001*M* Benzoquinone, 0·001*M* | Pt+

Temp.	25·4°		18°	
Minutes	30	60	90	120
Volt, I	0·0119	0·0119	0·0119	0·0119
„ II	0·0119	0·0119	0·0117	0·0117
	$\pi_{25°} = 0·7228.$		$\pi_{18°} = 0·7280.$	

Monochlorotoluhydroquinone.—Prepared by Schniter's method (*Ber.*, 1887, **20**, 2282), and crystallised from toluene and then twice from chloroform, the product had m. p. 172—174° (uncorr.). Schniter quotes m. p. 175° [0·2048 reduced 26·0 c.c. of 0·1002*N*-iodine, corresponding to 100·8% of $C_6H_2MeCl(OH)_2$. Cl, found = 22·26; calc. = 22·26%].

The hydrochloric acid used in the measurements was aerated with carbon dioxide.

TABLE X.

−Pt | Chlorotoluhydroquinone, 0·0005*M* Benzoquinone, 0·0005*M*; HCl 0·1*N*; Benzoquinhydrone | Pt+

Temp.	25°					
Minutes	10	40	100	150	175	1380
Volt, I	0·0217	0·0220	0·0222	0·0222	0·0223	0·0225
„ II	0·0214	0·0219	0·0223	0·0226	0·0227	0·0229
	Mean = 0·0224: $\pi_{25°} = 0·6542.$					

Dichlorotoluquinhydrone.—Prepared by oxidising the corresponding hydroquinone in 50% alcohol with the calculated quantity of ferric ammonium alum.

TABLE XI.

−Pt | Dichlorotoluquinhydrone; 0·1*N*-HCl; Benzoquinhydrone | Pt +

Temp.	25°							
Minutes	30	60	100	128	175	210	1110	1225
Volt, I	0·0394	0·0400	0·0406	0·0410	0·0415	0·0418	0·0425	0·0424
„ II	0·0382	0·0397	0·0400	0·0404	0·0407	0·0410	0·0424	0·0424
„ III	0·0382	0·0399	0·0400	0·0404	0·0408	0·0410	0·0424	0·0423
	$\pi_{25°} = 0·6566.$							

TABLE XII.

−Pt | Dichlorotoluquinhydrone, 0·0005*M*; 0·1*N*-HCl; Benzoquinhydrone | Pt+

Temp.	18°		
Minutes	20	30	45
Volt, I	0·0419	0·0419	0·0419
„ II	0·0419	0·0419	0·0419
„ III	0·0419	0·0419	0·0419
	$\pi_{18°} = 0·6625.$		

Monobromotoluhydroquinone.—To 5 g. of toluhydroquinone in 100 c.c. of ether and 45 c.c. of chloroform were added 6·45 g. of bromine in 82 c.c. of chloroform. The product (6·4 g.), recrystallised twice from toluene, melted at 176—178°. Clark (*Amer. Chem. J.*, 1892, **14**, 569) quotes 176—179°.

TABLE XIII.

$-Pt\left|\begin{matrix}\text{Monobromotoluhydroquinone, } 0{\cdot}0025M \\ \text{Benzoquinone, } 0{\cdot}0025M\end{matrix}\right.$; $\frac{\text{HCl}}{0{\cdot}1N}$; Benzoquinhydrone$\left|Pt+\right.$

25°.

Temp.					
Minutes	15	70	185	235	510
Volt, I	0·0209	0·0210	0·0212	0·0213	0·0214
„ II	0·0205	0·0206	0·0208	0·0208	0·0212

$\pi_{25°} = 0{\cdot}6564.$

Dibromotoluquinhydrone.—Prepared by oxidising 1 g. of monobromotoluhydroquinone in 5 c.c. of alcohol with 12·25 c.c. of 0·2*M*-ferric ammonium alum, the product was washed with water and dried between filter-paper (0·2003, titrated in presence of sodium bicarbonate with 0·0849*N*-iodine, required 11·75 c.c. Monobromotoluhydroquinone = 50·3%; calc. 50·0%).

TABLE XIV.

--Pt|Dibromotoluquinhydrone, 0·00125*M*; HCl 0·1*N*; Benzoquinhydrone|Pt+

25·2°.

Temp.				
Minutes	30	90	120	155
Volt, I	0·0397	0·0399	0·0399	0·0399
„ II	0·0397	0·0399	0·0399	0·0399

$\pi_{25°} = 0{\cdot}6591.$

Monochloroxylohydroquinone.—Prepared by the method of v. Rad (*Annalen*, 1869, **151**, 166) and Carstanjen (*J. pr. Chem.*, 1881, **23**, 430). 20 G. of *p*-xyloquinone were added to 200 c.c. of cold concentrated hydrochloric acid, a further 300 c.c. of acid were added, and the mixture was heated for 2—3 hours on the steam-bath. The crystals obtained on cooling were recrystallised from toluene, carbon tetrachloride, and twice from chloroform. Yield 7·75 g., m. p. 152—153° (Cl, found 20·81, calc., 20·56%).

TABLE XV.

$-Pt\left|\begin{matrix}\text{Monochloroxylohydroquinone, } 0{\cdot}002M \\ \text{Xyloquinone, } 0{\cdot}002M\end{matrix}\right.$; $\frac{\text{HCl}}{0{\cdot}1N}$; Benzoquinhydrone$\left|Pt+\right.$

25·4°.

Temp.			
Minutes	20	60	120
Volt, I	0·1069	0·1070	0·1069
„ II	0·1070	0·1069	0·1069

$\pi_{25°} = 0{\cdot}5949.$

Dichloroxyloquinhydrone.—1 G. of monochloroxylohydroquinone in 20 c.c. of water and 20 c.c. of alcohol was oxidised with 29 c.c. of 0·2*N*-ferric ammonium alum. The product was washed with water. Yield 0·7 g. (0·0993 reduced 5·85 c.c. of 0·0983 *N*-iodine. Monochlorohydroquinone found = 49·6, calc. = 50·0%).

TABLE XVI.

−Pt | Dichloroxyloquinhydrone; 0·1*N*-HCl; Benzoquinhydrone | Pt + 25·14°.

Temp.				
Minutes	30	65	125	150
Volt, I	0·1069	0·1070	0·1071	0·1071
„ II	0·1072	0·1073	0·1074	0·1074

$\pi_{25°} = 0·5918.$

The values of π given in Tables IV, V, XI, XII, XIV, and XVI are the results of direct determinations, whilst those given in the other tables (excluding I) are indirect values.

THE UNIVERSITY, COPENHAGEN. [*Received, August 23rd,* 1924.]

XXXIII.—*Hydrolysis of the* d-*Glucosides of* d- *and* l-*Borneol with Emulsin.*

By STOTHERD MITCHELL.

DAKIN (*J. Physiol.*, 1904, **30**, 253) found that when an optically inactive mixture of the two methyl mandelates was acted upon by the enzyme lipase the dextro-component was hydrolysed more rapidly than the lævo. Substitution of other alkyl groups for methyl produced differences in the relative rates of hydrolysis, and in order to investigate the effect of optically active groups he prepared *l*-menthyl mandelate and *d*-bornyl mandelate. Lipase, however, was without action on these compounds. Later (*ibid.*, 1905, **32**, 199), he succeeded in hydrolysing esters in which an asymmetric carbon atom was present in the alkyl group but not in the acid part of the molecule.

The hydrolysing action of emulsin on the *d*-glucosides prepared from the two forms of borneol has now been examined.

The *d*-borneol was obtained from commercial "borneol," which is a mixture of *d*-borneol and *l-iso*borneol resulting from the reduction of camphor (Pickard and Littlebury, J., 1907, **91**, 1977). The purified *d*-borneol and the *l*-borneol used had $[\alpha]^{20°}_{\text{Hg green}} = +42·14°$ and $-42·20°$, respectively, calculated from 15·4% solutions in alcohol.

The β-glucosides of *d*- and *l*-borneol were prepared by treating β-tetra-acetylbromoglucose in ether with an excess of borneol in

presence of silver carbonate, the acetyl groups being subsequently removed by means of barium hydroxide (Fischer and Raske, *Ber.*, 1909, **42**, 1473; Fischer, *Ber.*, 1916, **49**, 584; Hämäläinen, *Biochem. Z.*, 1913, **50**, 217).

Emulsin (2·5 g.) was mixed with 180 c.c. of water and kept in a thermostat at 37° for a day. The solution was filtered before use and gave $\alpha^{20°}_{Hg\ green} - 0{\cdot}64°$ ($l = 1$ dcm.).

A small quantity (0·3 g.) of each glucoside (which contains $1H_2O$) was placed in a 50 c.c. flask in a thermostat at 37°. The hydrolysis of the *d*-bornyl-*d*-glucoside was started by filling the flask to the mark with the emulsin solution, and an hour later the hydrolysis of the *l*-bornyl-*d*-glucoside was commenced. Two c.c. were removed at intervals and the amount of glucose present was determined by MacLean's method for estimating the sugar in blood (*Biochem. J.*, 1919, **13**, 135). The reaction constants are calculated from the usual formula for unimolecular reactions, $k = \{2{\cdot}30/(t_y - t_x)\} \log (c_x/c_y)$.

d-*Bornyl*-d-*glucoside*.				l-*Bornyl*-d-*glucoside*.			
Time in mins.	Glucose. Mg. in 2 c.c.	Glucoside. Mg. in 2 c.c.	$k \times 10^5$.	Time in mins.	Glucose. Mg. in 2 c.c.	Glucoside. Mg. in 2 c.c.	$k \times 10^5$.
270	0·70	10·13	10	180	0·87	9·83	34
330	0·77	10·01	9	303	1·12	9·39	33
515	0·82	9·92	11	361	1·22	9·22	33
613	0·89	9·80	10	435	1·33	9·03	35
860	1·03	9·55		673	1·74	8·31	
($= t_y$)		Average	10	($= t_y$)		Average	34

Hence emulsin hydrolyses *l*-bornyl-*d*-glucoside 3·4 times as rapidly as *d*-bornyl-*d*-glucoside. This is a striking example of the selective nature of enzyme action.

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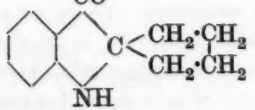
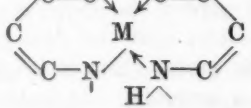
[*Received, November 24th*, 1924.]

XXXIV.—*Some Co-ordinated Compounds of the Alkali Metals.*

By NEVIL VINCENT SIDGWICK and SYDNEY GLENN PRESTON PLANT.

THE action of alkalis on ψ-indoxyl*spirocyclo*pentane (I) (Perkin and Plant, J., 1923, **123**, 676) has been examined and compounds of the type MB,HB [HB = (I); M = Li, Na, or K] obtained, which are soluble in toluene and behave as 4-covalent metallic compounds.

(I.) 

 (II.)

The Sodium Derivative.—Four grams of (I) were heated with sodium hydroxide (10 g.) in water (40 g.) in an air-tight steel tube at 210° for ½ hour. After cooling, the solid sodium derivative was washed out from the tube with aqueous sodium hydroxide (20%) and removed by filtration through asbestos. After drying on the steam-bath, it crystallised slowly from toluene in clusters of small, colourless prisms, melting at 204° to a cloudy liquid (Found: Na = 6·1. $C_{12}H_{12}ONNa$,$C_{12}H_{13}ON$ requires Na = 5·8%).

It is decomposed at once by water to re-form the indoxyl compound (I). When distilled in a vacuum, it gives a colourless distillate identical with (I); an infusible residue remains which yields (I) with dilute hydrochloric acid. Prolonged boiling with toluene causes a similar decomposition, with the separation of a colourless precipitate.

The Potassium Derivative.—Four grams of (I) were heated with 40 c.c. of aqueous potassium hydroxide (30%) in the steel tube for ½ hour at 200—210°. On pouring out, after cooling, the potassium compound appeared as an oil which soon solidified to a colourless mass. This separated from toluene in colourless plates melting to a cloudy liquid at 80—90° (Found: K = 9·6. $C_{12}H_{12}ONK$,$C_{12}H_{13}ON$ requires K = 9·5%). It gives (I) at once with water, and also on distillation, when it leaves an infusible residue; when it is boiled for a few minutes with toluene, a colourless precipitate separates.

The Lithium Derivative.—Four grams of (I) were heated with 40 c.c. of water saturated with lithium hydroxide at 15° for ½ hour in the steel tube at 200°. The product was washed out with lithium hydroxide solution, and removed by filtration through asbestos. After drying in a desiccator, it melted at 170° to a cloudy liquid [(I) melts at 113°] (Found: Li = 1·97. $C_{12}H_{12}ONLi$,$C_{12}H_{13}ON$ requires Li = 1·84%). It was decomposed by water to give the indoxyl compound. Attempts to recrystallise it from dry benzene, toluene, ligroin, and chloroform caused complete decomposition into this compound and a very small residue containing lithium.

Discussion of Results.

The action of alkali hydroxides, even in very large excess, on this indoxyl compound gives a substance MB,HB in which one metallic atom replaces one hydrogen atom in 2 mols. This loses 1 mol. of HB on heating, either alone or in toluene solution, forming, no doubt, the simple salt MB, which we should expect the indoxyl derivative to produce. There can be little doubt that the first product, MB,HB, contains a co-valent metallic atom. The indoxyl ring admits of co-ordination between a metal replacing the imide hydrogen and the carbonyl oxygen,

with the formation of the typical chelate ring of 6 atoms with two conjugate double links (see formula II), as in acetoacetic ester, acetylacetone, nitroso-β-naphthol, etc. (see Sidgwick, *Trans. Faraday Soc.*, 1923, **19**, 474). The strong tendency of the alkali metals to ionise will prevent the formation of this ring in the simple derivatives MB, which therefore are salts; but the greater stability secured by the completion of four non-polar links causes these compounds to add a second molecule of the indoxyl derivative (without replacement of hydrogen), giving the structure II.

The remarkable solubility in toluene is thus explained, since the compound is not a salt. The sodium has its octet completed by means of three pairs of shared electrons borrowed from the two oxygens and the now quadrivalent nitrogen. The second ring, being attached only by co-ordinate links, is easily removed, and hence the compound dissociates on heating.

The potassium compound is precisely similar in behaviour, although it has a markedly lower melting point (80—90° instead of 204°). Lithium seems to form an analogous compound, m. p. 170°, but owing to its great instability this could not be purified.

These appear to be the first recognised co-ordination compounds of sodium and potassium.

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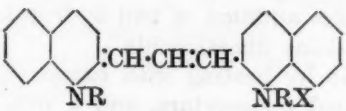
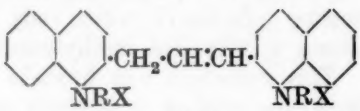
XXXV.—*Reduction of the Carbocyanines.*

By FRANCES MARY HAMER.

THE constitution (I) of carbocyanine was deduced from general considerations, supported by analytical evidence, and established by the study of the oxidative breakdown of pinacyanole (Mills and Hamer, J., 1920, **117**, 1550). The prediction of similar classes of dyes, with the nuclei linked in the 4 : 4′- and 2 : 4′-positions, respectively, has now been fulfilled (Mills and Braunholtz, J.,



(I.)

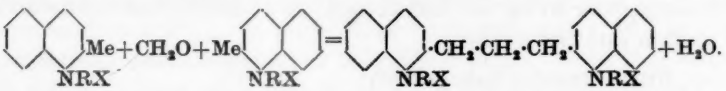


(II.)

1923, **123**, 2804; Mills and Odams, J., 1924, **125**, 1913), thus confirming the formula.

Two syntheses have been adduced in its support. König's (*Ber.*, 1922, **55**, 3293) consists in condensation of quinaldine alkyl-

halide with orthoformic ester in presence of acetic anhydride. It is not obvious why this is considered to throw more light on the constitution of carbocyanine than does the earlier preparation by the action of formaldehyde on an alcoholic solution of quinaldine alkylhalide in presence of alkali (Mills and Hamer, *loc. cit.*). The synthesis by means of orthoformic ester does, however, differ from the latter, as from the preparation in which the formaldehyde is replaced by a trihalogenmethane (D.R.-P. 200,207), in that a 50% yield of analytically pure product is claimed. But when König's procedure was repeated, it was found that even twice the quoted amount of acetic anhydride was barely sufficient for solution of the given quantity of quinaldine ethiodide, and that the considerable yield of crude product consisted chiefly of impurities. The method is said to be equally applicable to the more soluble methiodide, but when this was used in order that the directions might be followed exactly, the yield of pure carbocyanine was not more than 10%. In the second synthesis (Hamer, J., 1923, **123**, 246), methylenediquinaldine dialkylhalide was prepared from quinaldine alkylhalide and formaldehyde according to the equation:



The action of alkali, in presence of quinoline alkylhalide, eliminated halogen acid with, apparently, simultaneous removal of two hydrogen atoms, since carbocyanine (I) was directly formed. This synthesis proves the existence of a three-carbon chain joining the quinoline nuclei of the carbocyanine molecule, and is unequivocal except for the unexplained fact that the presence of quinoline alkylhalide is necessary.

The converse transformation of carbocyanine into methylenediquinaldine dialkylhalide has now been accomplished, thus clearly demonstrating the relationship. The addition of hydriodic acid (b. p. 126°) to 1 : 1′-dimethylcarbocyanine iodide gave yellow crystals, too unstable to isolate for analysis, but doubtless possessing formula II, which only requires addition of two hydrogen atoms to represent methylenediquinaldine dimethiodide.

This reduction was brought about by heating with excess of hydriodic acid at a carefully regulated temperature, and a 78% yield of methylenediquinaldine dimethiodide was the result. Similarly, 1 : 1′-diethylcarbocyanine iodide and 6 : 6′-dimethyl-1 : 1′-diethylcarbocyanine iodide were reduced to methylenediquinaldine diethiodide and 6 : 6′-dimethylmethylenediquinaldine diethiodide, respectively. The temperature is an important factor in the

reduction, since with a lowering of a few degrees, unchanged carbocyanine remains, whilst too high temperatures lead to decomposition of the dialkylhalide.

p-Dimethylaminobenzylidenequinaldine ethiodide was similarly heated with hydriodic acid, but analysis of the product proved that, besides reduction of the ethylenic linking, the two methyl groups had been replaced by hydrogen atoms. That the compound was *p*-aminobenzylquinaldine ethiodide, and not the hydriodide of *p*-dimethylaminobenzylidenequinaldine, was established by the fact that it was neutral and unattacked by ammonia.

Experimental.

Preparation of 1 : 1′-*Dimethylcarbocyanine Iodide by Use of Orthoformic Ester* (compare König, *loc. cit.*).—Quinaldine methiodide (6 g.) was boiled with acetic anhydride (60 c.c., b. p. 135—140°), and during 5 minutes orthoformic ester (2·1 g., b. p. 142—146°) was added. The mixture was concentrated to half volume and the solid removed when cold. The greater part of the impurity was extracted by boiling methyl alcohol (15 c.c.), and the undissolved crude carbocyanine was recrystallised from methyl alcohol (yield 6% instead of 50). The method recommended in a later paper (*Ber.*, 1924, **57**, 685) gave a 10% yield.

Reduction of 1 : 1′-*Dimethylcarbocyanine Iodide.*—By heating the carbocyanine (1·5 g.) with hydriodic acid (10 c.c., b. p. 126°) in a sealed tube at 182—185° for 6 hours, black crystals of periodide were produced; addition of water gave a yellow precipitate. The total solid was suspended in boiling 1·5% hydrochloric acid, and sulphur dioxide passed in until a clear solution was obtained, when potassium iodide was added (1·5 g.). The product (yield 78%) was recrystallised from dilute hydrochloric acid, with charcoal treatment and addition of potassium iodide. The crystals were ground with pyridine (5 c.c.) to remove any acid impurity (see below), washed with acetone, recrystallised from absolute alcohol, and dried in the steam-oven (Found: C = 47·27; H = 4·19; I = 43·41. Calc. for $C_{23}H_{24}N_2I_2$, C = 47·42; H = 4·16; I = 43·61%); m. p. 207° (decomp.), alone or mixed with methylenediquinaldine dimethiodide. The compound had the properties of this substance and its crystallisation could be started by inoculation with it.

By reduction of the carbocyanine at 203—209°, the iodide obtained after two recrystallisations from absolute alcohol was strongly acid; it appeared to be free from methylenediquinaldine dimethiodide, since it was completely and easily soluble in cold pyridine, in which the dimethiodide is practically insoluble.

Reduction of 1 : 1′-*Diethylcarbocyanine Halide.*—The iodide or bromide (1 g.) was heated with hydriodic acid (7 c.c.) at 178—181° and on reduction of the resultant periodide, the crystalline product (yield 76%) was almost pure (Found: I = 41·27%). It was treated with pyridine and recrystallised from absolute alcohol (yield 54%). This reduction product, methylenediquinaldine diethiodide, and their mixture, melted simultaneously at 205° (decomp.). For analysis, it was dried in the steam-oven (Found: C = 48·80; H = 4·73; I = 41·62. Calc. for $C_{25}H_{28}N_2I_2$, C = 49·18; H = 4·63; I = 41·61%).

Reduction of 6 : 6′-*Dimethyl*-1 : 1′-*diethylcarbocyanine Iodide.*—Hydriodic acid (5 c.c.) and the carbocyanine (0·5 g.) [fine needles of the almost colourless hydriodide formed] were heated at 178—185° for 5 hours and the solid was treated with sulphur dioxide as in other cases (yield 83%). For analysis, the iodide was dried over sulphuric acid and soda-lime (Found: I = 38·97. Calc. for $C_{27}H_{32}N_2I_2,H_2O$, I = 38·68%). It melted at 219°, alone or mixed with 6 : 6′-dimethylmethylenediquinaldine diethiodide. The m. p. was unaltered by recrystallisation.

Reduction of p-*Dimethylaminobenzylidenequinaldine Ethiodide.*—This was prepared by the method of König and Treichel (*J. pr. Chem.*, 1921, [ii], **102**, 63). By increasing the time of heating from 1 hour to 24 hours, the yield of recrystallised product was raised from 23 to 76% (Found: I = 29·33; calc. 29·51%); m. p. 259—263° (decomp.).

p-Dimethylaminobenzylidenequinaldine ethiodide (1·5 g.) and hydriodic acid (10 c.c.) were heated for 3 hours at 178—181°, water was added, and the solid, in boiling dilute hydrochloric acid, treated with sulphur dioxide. The clear solution gave no precipitate with potassium iodide (1·5 g.); but ammonia produced an orange tar which hardened, and was powdered, filtered, and dried in a vacuum desiccator. From absolute alcohol, it separated as clear red crystals (yield 59%). A thrice recrystallised specimen was dried in a vacuum desiccator and was shown by analysis to be *p*-aminobenzylquinaldine ethiodide (Found: C = 56·64; H = 5·26; N = 7·08; I = 31·30. $C_{19}H_{21}N_2I$ requires C = 56·41; H = 5·24; N = 6·93; I = 31·41%). It is moderately soluble in alcohol or water; m. p. 200—201°, with incipient softening a couple of degrees lower.

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XXXVI.—*Fission of the Pyridine Nucleus during Reduction. Part II. The Preparation of Glutardialdoxime.*

By Brian Duncan Shaw.

The suggestion (J., 1924, **125**, 3041) that the initial product of the action of sodium and alcohol on pyridine is 1 : 4-dihydropyridine has now been confirmed, for, although this has not been isolated, if the solution is treated with hydroxylamine, ammonia is evolved, and a good yield (70%) of glutaraldehydedioxime obtained. This value is obviously too low, since some of the dihydro-compound is further reduced. The initial reduction product, therefore, is largely, if not entirely, 1 : 4-dihydropyridine.

Further work on glutardialdehyde and its homologues is in progress.

Experimental.

Pyridine, b. p. 115—116°, was heated at 80° with 4% potassium permanganate solution until a pink colour persisted. The purified base was separated by distillation, dried over caustic soda, and boiled with powdered calcium carbide. The alcohol was boiled with powdered calcium carbide and fractionated through a column filled with freshly-broken lumps of the same material.

Glutardialdoxime.—No ammonia was evolved when pyridine (80 g.) in boiling alcohol (400 c.c.) was treated with sodium (24 g.). Hydroxylamine hydrochloride (36 g.) in dry alcohol was added, and the mixture boiled for a few minutes, when ammonia was evolved copiously. The remainder of the sodium was precipitated by addition of the requisite quantity of hydrochloric acid diluted with alcohol. After 2 hours' boiling, the sodium chloride was removed and the filtrate distilled until only 80 c.c. remained. The oxime separated slowly and a further quantity was obtained from the mother-liquor (yield 28 g. or 65% calculated on the hydroxylamine); m. p. 175° after recrystallisation from water or pyridine. It may be sublimed without decomposition. Its identity was established by analysis (Found: N = 21·2; calc. 21·05%), by its reactions, and by reduction to pentamethylenediamine (some piperidine was also produced). Boiling with hydrochloric acid gave pyridine (compare Braun and Danziger, *Ber.*, 1913, **46**, 103). When amyl alcohol was used for the reduction, little hydrogen was evolved, and the yield, calculated on the assumption that the sodium liberated the theoretical quantity of hydrogen and that only 1 : 4-dihydropyridine was produced, varied from 68—72%. Excess of hydroxylamine was used in these cases.

Glutardialdehyde was obtained from the oxime by the method used by Harries in the case of succindialdehyde. Both the glass-like polymeride and the unimolecular form described by Harries and Tank (*Ber.*, 1908, **41**, 1705) were obtained.

Part of this work was carried out at University College, Nottingham. The author is indebted to Professor F. S. Kipping, F.R.S., for his kindness during that period, to the Department of Scientific and Industrial Research for a maintenance grant, and to the South Metropolitan Gas Company for the supply of pyridine.

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UNIVERSITY OF LONDON. [*Received, November 19th*, 1924.]

XXXVII.—*The Action of Bromine on Sodium and Silver Azides.*

By DOUGLAS ARTHUR SPENCER.

Part I. Bromoazoimide.

DURING the course of experiments, suggested by Professor H. B. Baker, aiming at the preparation of triatomic nitrogen, bromine vapour, diluted with nitrogen, was passed over sodium azide. The colour of the gaseous mixture faded considerably, but was not completely discharged however long the bromine remained in contact with the azide, and the gas leaving the apparatus had a pungent but sickly smell reminiscent of hydrazoic acid and dilute bromine vapour.

An aqueous solution of the gas was yellow, gave a blood-red coloration with ferric chloride, smelled of hypobromous and hydrazoic acids, and slowly evolved nitrogen on standing.

Preliminary attempts to freeze out any compound formed resulted in violent explosions which occasionally detonated the sodium azide. The dilute gas mixture is itself extremely sensitive to shock or rise of temperature, the explosion being accompanied by a flash of livid blue light whilst the glass parts of the apparatus are reduced to powder.

The analysis was therefore performed indirectly as follows: Pure carbon dioxide, generated by the action of boiled-out hydrochloric acid on calcite, was washed with sodium bicarbonate and dried by sulphuric acid and phosphorus pentoxide, and was used to carry bromine vapour (derived from the liquid at 5°) over a large surface of sodium azide, contained in a glass tube 175 cm. long and 0·5 cm. in diameter, coiled into a spiral and kept at 0°.

The gas current was adjusted to carry about 0·05 g. of bromine over the azide per hour. The pale yellow gas so obtained was passed through a hard glass tube, 10 cm. long, packed with glass fragments and heated at the far end by a small bunsen flame. By this means, the compound was decomposed without explosion and the gas acquired the much darker red colour characteristic of bromine vapour. The products of decomposition were passed over silver leaf into a potash nitrometer, the carbon dioxide stream being stopped when the volume of gas in the latter had remained constant for ½ hour. The volume of this gas, which was pure nitrogen having the normal density, was measured over water and reduced to that at *N.T.P.* The excess of silver leaf was dissolved in nitric acid and the silver bromide determined gravimetrically. The results are tabulated below.

TABLE I.

Expt. No.	Duration in hours.	Bromine taken (g.).	Bromine recovered (g.).	C.c. of N_2 obtained.	$N_3 : Br_x$. x.
1	2	0·1684	0·1247	37·07	1·41
2	5½	0·3938	0·2128	74·10	1·26
3	2½	—	0·1549	57·60	1·13
4	4½	0·1935	0·09447	36·00	1·11
5	6½	0·1701	0·0802	28·80	1·14
6	9½	0·2906	0·1324	50·00	1·13
7	10½	0·3833	0·1706	61·65	1·15

Excluding the results of experiments 1 and 2, in which the bromine vapour was in contact with the azide for a comparatively short period, the mean value is $N_3 : Br_{1·13}$.

Whilst pointing to the presence of *bromoazoimide*, N_3Br, the analyses show that there is about 8% more bromine in the gas than is required by the simple formula. Since the quantity of bromine recovered agrees with that required by the equation $NaN_3 + Br_2 = NaBr + N_3Br$, it was at first thought that this excess was due to a deficiency in the volume of nitrogen obtained, but the density, viscosity and chemical behaviour of the nitrogen were normal and therefore it is improbable that any polymeric modification was present, even if it could have survived the heating. A second possibility was that the reaction was reversible or incomplete, but alterations in the temperature of the reaction tube, and of the time of contact of the bromine with the sodium azide, did not materially affect the final analysis. The formation of some other nitrogen bromide, *e.g.*, NBr_3, was a third possibility.

By using a fine capillary tube as connecting link between the reaction tube and condensing vessels, any explosion could be localised, and, by immersing these vessels in freezing mixtures kept in unsilvered Dewar flasks standing in large beakers of water, rendered less dangerous. It then became possible to freeze the substance

out, and to fractionate it by passing a stream of nitrogen over the surface whilst allowing the temperature to rise.

The analysis of these fractions was carried out as follows : The vapour derived from each fraction was absorbed in standardised solutions of carbonate-free caustic soda containing hydrogen peroxide. With this mixture the compound forms sodium azide and sodium bromide, the hydrogen peroxide reducing the sodium hypobromite first formed :

$$N_3Br + 2NaOH = NaBrO + NaN_3 + H_2O.$$
$$NaBrO + H_2O_2 = NaBr + H_2O + O_2.$$

By titrating the excess of sodium hydroxide with $N/10$-sulphuric acid and phenolphthalein, the amount of alkali required to combine with the N_3 and Br radicals was found. A known excess of silver nitrate was then added, silver bromide and azide being precipitated. The mixture was boiled with nitric acid until all the silver azide had been decomposed and the hydrazoic acid driven off. The cooled solution was titrated with ammonium thiocyanate, giving a measure of the silver nitrate required to precipitate the bromide present.*

The results are summarised in Table II.

TABLE II.

Expt.	Fraction.	*a*.	*b*.	*t*.	$N_3 : Br_x$. *x*.
1	1st	91·80	48·30	−10°	1·06
	2nd	84·70	43·70	+ 5	1·07
2	1st	117·9	58·06	−18	0·97
	2nd	58·55	32·71	+ 5	1·26
3	1st	29·04	14·73	−20	1·036
	2nd	52·17	27·19	−10	1·09
	3rd	90·51	50·67	+ 5	1·18

a = c.c. of $N/10$-NaOH neutralised = N_3 + Br; b = c.c. of $N/10$-$AgNO_3$ required to neutralise Br; t = temperature below

* The above procedure provides a method for the estimation of soluble azides in presence of halides which has decided advantages over the gravimetric determination (Dennis and Isham, *J. Amer. Chem. Soc.*, 1907, **29**, 18). Owing to the number of operations involved, and the appreciable solubility of silver azide at normal temperatures, the latter method is tedious and liable to error, the results being usually low. On the other hand, the volumetric method—titration with silver nitrate followed by treatment with nitric acid and thiocyanate—is both rapid and trustworthy if the solution is first rendered barely acid by the addition of sodium acetate and acetic acid. If potassium arsenate is used as indicator in the first titration, the final acid solution is colourless. The colour of silver arsenate is, however, not so intense as that of the chromate, and quite accurate results may be obtained with the latter. Owing to the solution being slightly acid with acetic acid, a small amount of dichromate is formed and the solution is of a yellow-orange colour rather than the usual bright yellow, and the use of a comparison basin is advisable.

which the fraction was obtained. C.c. of $N/10$-NaOH equivalent to $N_3 = a - b$.

The first fractions (with a mean value of $N_3 : Br_{1\cdot02}$) were dark orange-red liquids which solidified at about −45° to dark red solids. The later fractions were ruby red, but even these were distinctly lighter and apparently much more mobile than liquid bromine.

If the high bromine content is due to the presence of free bromine, it should be possible to remove this by treating the liquid with sodium azide. A first fraction, obtained at −15°, was distilled on to sodium azide kept at −25°. The colour of the liquid was not altered, even after 3 hours' contact (Found : $N_3 : Br_{1\cdot04}$). Also when gas derived directly from the apparatus and of approximate composition $N_3Br_{1\cdot13}$ (see Table I) was condensed on to sodium azide, and, after 3 hours, the liquid was allowed to vaporise, the proportions were $N_3 : Br_{1\cdot16}$. The excess of bromine, therefore, is not present in the free state and the most probable explanation is that it is in the form of nitrogen tribromide, NBr_3. When the gas was passed into water the solution contained, in addition to hydrazoic and hypobromous acids, traces of ammonium salts. This cannot, however, be taken as a proof of the presence of NBr_3, for Hantzsch states that iodoazoimide (triazo iodide) gives rise to a small quantity of ammonia on hydrolysis (compare L. Spiegel, "Der Stickstoff," 1903, pp. 35, 36).

Hantzsch (*Ber.*, 1900, **33**, 522), by the interaction of silver azide (but not potassium azide) and iodine in ether solution at 0° and evaporation of the ether, obtained red crystals of the highly unstable iodoazoimide, N_3I (which he states is probably colourless when pure). A freshly prepared aqueous solution is neutral towards litmus and starch, but hydrolyses fairly rapidly to hydrazoic and hypoiodous acids. In non-aqueous solvents, the compound slowly decomposes to iodine and nitrogen.

When either sodium or silver azide is treated with bromine dissolved in ether, benzene, or ligroin, bromoazoimide is formed, but the method is not a convenient one. The bromine attacks the solvent to a certain extent and, owing to the great solubility and volatility of bromoazoimide, it is impossible to separate it from the solvent. Moreover, the presence of traces of water results in the immediate hydrolysis of the compound to hydrazoic and hypobromous acids. This is most striking in the case of silver azide–bromine mixtures, as the admission of a drop of water results in a vigorous evolution of nitrogen due to the rapid reaction of the hypobromous acid at once produced, with the silver azide.

Properties of Bromoazoimide.—The purest sample of the bromide obtained in these experiments was a mobile, very volatile, orange-

red liquid, which changed to a dark red solid at about −45°. The pungent vapour has toxicological properties similar to hydrazoic acid, causing giddiness, headache, and a slackening of the muscles when inhaled. Traces of the vapour irritate the eyes and cause a slight difficulty in breathing, due apparently to congestion of the nasal mucous membrane.

Solid, liquid, and vapour are as sensitive to shock as iodoazoimide, the explosion (often apparently spontaneous) being accompanied by a flash of livid blue light. Some idea of the instability of the compound, even at −200°, may be gathered from the fact that, of twenty-four attempts at freezing the compound and determining its melting point, only six were completed without explosion. Fortunately, in the majority of cases, the sphere of action was limited to a radius of about 3 feet. Within this radius, all glass apparatus was reduced to powder; beyond it, a reinforced glass screen proved a sufficient protection. The liquid explodes in contact with phosphorus, arsenic, sodium, and silver foil, but the vapour, when diluted with nitrogen and passed over silver leaf or sodium, gives a film of the corresponding azide and bromide.

The liquid is apparently miscible in all proportions with ether, but is less soluble in benzene or ligroin. These solutions are stable for a few hours in the dark, but, when concentrated, are liable to explode on shaking, and on standing gradually decompose, giving nitrogen and bromine, the latter attacking the solvent. When passed into water, bromoazoimide hydrolyses instantaneously, giving a mixture of hydrazoic and hypobromous acids, and the solution, on standing, evolves nitrogen by the interaction of these acids. When bromoazoimide is passed into potassium iodide solution, iodine is liberated equivalent to the hypobromous acid produced and potassium azide is obtained :

$$N_3Br + 2KI = KN_3 + KBr + I_2.$$

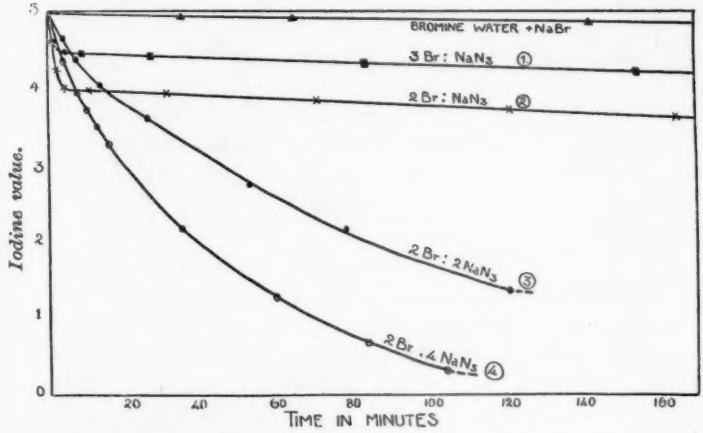
This experiment was performed by substituting a potassium iodide absorption vessel for the heated glass decomposition tube in the apparatus described on p. 216, and it is possibly significant that 6 c.c. of nitrogen collected in the nitrometer. Some of this nitrogen may have been due to a slight decomposition of the bromoazoimide into its elements before it reached the absorption vessel, but in view of the fact that no free bromine was detected when the compound was distilled on to sodium azide (p. 219), this does not seem probable. It is thought, therefore, that the nitrogen may have been derived from NBr_3 present.

Part II.

Since bromoazoimide is instantly hydrolysed by water, the reaction in aqueous solution between bromine and sodium azide should yield hydrazoic and hypobromous acids, and therefore should differ from that between iodine and sodium or potassium azide, which occurs only in presence of sulphur compounds, yielding nitrogen (Raschig, *Chem. Ztg.*, 1908, **32**, 1203; Browne, *J. Amer. Chem. Soc.*, 1922, **44**, 2106).

When sodium azide solution was added to *N*/10-bromine water, the colour of the mixture faded at once to a pale straw-yellow and nitrogen was evolved at a rate depending on the concentration, temperature, and proportions of the solutions. Approximately

FIG. 1.



94% of the expected volume of nitrogen was evolved in 15 hours from concentrated solutions at the ordinary temperature. The gas was contaminated with oxygen, hydrazoic acid, and hypobromous acid.

The course of the reaction with various proportions and concentrations of the reactants can conveniently be followed by plotting the fall in iodine value of the solution against time.

Aliquot portions of the effervescing solution, removed at fixed intervals, were added to potassium iodide, and the iodine liberated by the hypobromous acid was titrated with *N*/10-sodium arsenite (thiosulphate is unsuitable, as it causes an instantaneous liberation of all the available nitrogen. Browne, *loc. cit.*).

In the figure, typical curves obtained with *N*/10-solutions at 15° are plotted.

Hypobromous acid reacts somewhat slowly with hydrazoic acid,

but rapidly with sodium azide solutions (the latter are always alkaline by hydrolysis, and sodium hypobromite is dissociated to a greater extent than hypobromous acid). Curves 1 and 2 correspond therefore to the slow fall in concentration of hypobromous acid with hydrazoic acid, and curves 3 and 4 to the fall in the presence of an excess of sodium azide.

An abrupt change in the slope of the curves occurs when one uses more than one equivalent of sodium azide to two of bromine.

$$NaN_3 + Br_2 + H_2O = NaBr + HN_3 + HBrO \quad . \quad . \quad (1)$$
$$HBrO + 2HN_3 = HBr + H_2O + 3N_2 \quad . \quad . \quad . \quad (2)$$

Since one equivalent of hypobromous acid can decompose two equivalents of hydrazoic acid, there is, in the solution, sufficient hypobromous acid to decompose a further equivalent of sodium azide :—

$$HBrO + 2NaN_3 = NaBr + NaOH + 3N_2 \quad . \quad . \quad . \quad (3)$$

Equivalent proportions of sodium azide solution and bromine water were mixed. After 17 hours, gas evolution had ceased and the solution was colourless and exactly neutral :—

$$NaN_3 + Br_2 + H_2O = NaBr + HBrO + HN_3 \quad . \quad . \quad (1)$$
$$NaN_3 + HBrO + HN_3 = NaBr + H_2O + 3N_2 \quad . \quad . \quad (4)$$

One equivalent of sodium azide was mixed with two equivalents of bromine water. The effervescence was much slower, resembling that obtained when mixtures of hydrazoic and hypobromous acids react in presence of sodium bromide.

$$NaN_3 + Br_2 + H_2O = NaBr + HBrO + HN_3 \quad . \quad . \quad (1)$$
$$HN_3 + \tfrac{1}{2}HBrO = \tfrac{1}{2}HBr + \tfrac{1}{2}H_2O + 1\tfrac{1}{2}N_2 \quad . \quad . \quad . \quad (2)$$

The solution should therefore contain equal parts of hydrobromic and hypobromous acids amounting to one equivalent at the conclusion of the experiment.

The nitrogen evolved would be expected to carry away the greater part of these volatile acids and yet, after 17 hours, the solution still contained a little more than a quarter of an equivalent of acid, one-half of which consisted of hypobromous acid, the other half being presumably hydrobromic acid, since there was only the slightest trace of azoimide.

The Reaction between Bromine Water and Silver Azide.—Silver azide, precipitated from a solution of sodium azide slightly acidified with nitric acid, was washed until free from soluble silver salts and treated with freshly-prepared bromine water. A vigorous

reaction took place and silver bromide was obtained (in daylight, the yellow precipitate at once commenced to turn slate-blue unless excess of bromine was present). The evolved gas contained traces of azoimide together with about 1% of oxygen, but no nitrogen oxides, and after drying with lime and phosphorus pentoxide, had the density of ordinary nitrogen.

About 92% of the nitrogen expected from the equation $2AgN_3 + Br_2 = 2AgBr + 3N_2$ was obtained within 10 minutes of the mixing, but the presence of hydrazoic acid and oxygen suggests that the side reaction $AgN_3 + Br_2 = AgBr + N_3Br$ probably occurs in a manner analogous to the formation of iodoazoimide (Hantzsch, *loc. cit.*). The bromoazoimide was instantly hydrolysed by the water, the oxygen being derived by decomposition of the hypobromous acid thus produced (compare Fleury, *Compt. rend.*, 1920, **171**, 957). The formation of hydrazoic acid in this manner accounts for the deficiency in nitrogen, as azoimide is only slowly attacked by hypobromous acid; the latter moreover reacts very rapidly with silver azide.

Summary.

In the absence of water, bromine reacts with sodium and silver azides to give the highly unstable bromoazoimide:

$$XN_3 + Br_2 = XBr + N_3Br.$$

This compound (m. p. about −45°), whilst resembling iodoazoimide in its general properties, differs in its greater volatility and immediate decomposition by water.

Bromine water reacts instantly with sodium azide solutions to give a mixture of hydrazoic and hypobromous acids, which then interact to produce nitrogen. When the sodium azide is present in larger quantities than are required by the equation $NaN_3 + Br_2 + H_2O = NaBr + HN_3 + HBrO$, the nitrogen evolution is more rapid owing to the interaction of the hypobromous acid with the excess of sodium azide, and it is for this reason that two equivalents of bromine are able to decompose two equivalents of sodium azide.

The reaction between silver azide and bromine water differs from that with iodine solutions in that it is better represented by the equation

$$2AgN_3 + Br_2 = 2AgBr + 3N_2.$$

The only evidence for the momentary existence of bromoazoimide in aqueous solution is the formation of a certain amount of azoimide with consequent loss of free nitrogen.

The density or viscosity of all nitrogen samples was determined,

but no indication of the existence of the polymeride N_3 was obtained.

My thanks are due to Professor H. B. Baker, at whose suggestion, and under whose supervision, the work has been carried out.

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LONDON, S.W. 7. [*Received, November 15th*, 1924.]

XXXVIII.—*The Constitution of Disulphoxides. Part II.*

By CECIL JAMES MILLER and SAMUEL SMILES.

ALTHOUGH the symmetrical structure of the disulphoxides (I) has been generally accepted, the evidence adduced in its favour has been incorrectly interpreted and is in fact ambiguous, and many simple reactions of these substances appear clearly to indicate the thiosulphonate structure (II), such, for example, as their behaviour with zinc dust, potassium sulphide, sodium arsenite, and mercaptans (J., 1924, **125**, 176). Moreover, this view is supported by syntheses of disulphoxides from sulphenic halides and silver sulphinates (Zincke, *Annalen*, 1912, **391**, 67). Since all the definite evidence thus favoured the thiosulphonate structure, it was concluded that this should not be abandoned, but instead should be regarded as the most probable until final proof of one structure or another was forthcoming.

(I.) $Ar\cdot\overset{\displaystyle O}{\overset{\|}{S}}\cdot\overset{\displaystyle O}{\overset{\|}{S}}\cdot Ar$ $\qquad$ $Ar\cdot SO_2\cdot S\cdot Ar$ (II.) $\qquad$ $Ar\overset{\displaystyle O}{\overset{\|}{S}}\cdot O\cdot SAr$ (III.)

The experiments now described provide the necessary further proof of this unsymmetrical constitution, in that (1) the action of Grignard's reagent with the disulphoxides must be added to those already quoted as indicating this structure, (2) the reduction of disulphoxides with hydrogen iodide, which hitherto has been quoted as the main evidence for the symmetrical formula, is not only useless as such, but accords with the thiosulphonate structure, (3) the unsymmetrical character of the disulphoxides is demonstrated by synthesis.

Although the behaviour of numerous carbon compounds of sulphur with alkyl and aryl magnesium halides has been investigated (Lapworth, J., 1912, **101**, 297; Hepworth and Clapham, J., 1921, **119**, 1188; Wedekind, *Ber.*, 1921, **54**, 1604), that of the disulphoxides appears to have escaped attention. These substances are very readily attacked by the magnesium compounds, and, using

equimolecular proportions of the reactants, high yields of the sulphinic acids have been isolated, fission of the disulphoxide taking place apparently according to the following scheme (IV):

$$\text{(IV.)}\quad \begin{matrix} \text{Ar}\cdot\text{SO}_2\cdot\text{S}\cdot\text{Ar} \\ \text{IMg}\cdot\text{R} \end{matrix} \qquad\qquad \begin{matrix} \text{Ar}\cdot\text{SO}\cdot\text{SO}\cdot\text{Ar} \\ \text{IMg}\cdot\text{R} \end{matrix} \quad \text{(V.)}$$

The sulphinic acid was obtained in every case examined, but the fate of the thioaryl group of the disulphoxide varied according to the nature of the magnesium compound used: with magnesium methyl iodide, the methyl aryl sulphide, $\text{Ar}\cdot\text{S}\cdot\text{CH}_3$, was commonly obtained, whilst with magnesium phenyl iodide the disulphide and diphenyl also were observed. The chief point at issue is the situation of the oxygen in the molecule of the disulphoxide, and with the symmetrical formula it is very difficult to explain the isolation of 80% of this as sulphinic acid. According to this symmetrical constitution, it would be expected that fission of the molecule would result in the formation of a sulphoxide (V), but this has not been observed. The results of this decomposition evidently support the unsymmetrical structure and appear inexplicable on the basis of the symmetrical formula. The mode of experiment is described and the results are tabulated on subsequent pages.

The fact that the disulphoxides are easily reduced by hydrogen iodide to disulphides has been regarded as sufficient reason for rejecting the thiosulphonate structure and as proving the presence of the true disulphoxide arrangement (Hinsberg, *Ber.*, 1908, **41**, 2836, 4294; 1909, **42**, 1278; Fries, *Ber.*, 1914, **47**, 1195). It is assumed that the reduction is direct, and since the sulphonyl group usually is not easily reduced by this reagent whilst the thionyl group is readily attacked, the conclusion would seem justified, but it has been pointed out (Smiles and Gibson, J., 1924, **125**, 176) that the force of the argument depends on the assumption that reduction is direct and is not accompanied by fission of the molecule. If, however, rupture does take place, the reduction cannot be used as an argument against the unsymmetrical or in favour of the symmetrical formula, for in either case a disulphide must be expected as the final product of the reaction. The question whether this fission takes place or not may be answered by the reduction of a disulphoxide containing different aromatic groups. In such a case, if the unsymmetrical disulphide is the sole product (VI), the assumption of direct reduction is clearly justified, but if both, or even one, of the symmetrical disulphides are obtained (VII) it must be admitted that rupture of the dithio-system has taken place.

$$\text{(VI.)}\quad \text{R}^1\cdot\text{SO}\cdot\text{SO}\cdot\text{R}^2 \longrightarrow \text{R}^1\cdot\text{S}\cdot\text{S}\cdot\text{R}^2$$

$$\text{(VII.)}\quad 2\text{R}^1\cdot\text{S}_2\text{O}_2\cdot\text{R}^2 \longrightarrow (\text{R}^1\text{S})_2 + (\text{R}^2\text{S})_2$$

Disulphoxides containing different aromatic nuclei are readily prepared by an extension of the synthetical method of Zincke (*loc. cit.*) For example, when the silver salts of *p*-toluenesulphinic acid and *p*-chlorobenzenesulphinic acid are treated with *o*-nitrophenylsulphur chloride, the *o-nitrophenyl* p-*toluenethiolsulphonate* (VIII) and o-*nitrophenyl* p-*chlorobenzenethiolsulphonate* (IX) are respectively formed.

$$NO_2{\cdot}C_6H_4{\cdot}SCl + AgSO_2{\cdot}C_7H_7 = AgCl + NO_2{\cdot}C_6H_4{\cdot}S{\cdot}SO_2{\cdot}C_7H_7.$$
(VIII.)

$$NO_2{\cdot}C_6H_4{\cdot}SCl + AgSO_2{\cdot}C_6H_4Cl = AgCl + NO_2{\cdot}C_6H_4{\cdot}S{\cdot}SO_2{\cdot}C_6H_4Cl$$
(IX.)

Reduction of these substances with hydrogen iodide in the usual manner (compare Hinsberg, *loc. cit.*) furnished *o*-nitrophenyl disulphide, $(NO_2{\cdot}C_6H_4{\cdot}S{\cdot})_2$, in good yield and in the case of the chloro-derivative *p*-chlorophenyl disulphide also was isolated. Hence it is clear that the disulphoxide system has been broken during the process of reduction and the reaction cannot be admitted as evidence favouring the symmetrical and excluding the unsymmetrical structure. Nothing else can be deduced from this result, but further information has been gained by adopting milder conditions of reduction with hydrogen iodide or by the use of dilute hyposulphite (in presence of sodium carbonate). The derivative (VIII) then yielded *p*-toluenesulphinic acid and the nitrophenyl disulphide, the chloronitro-derivative (IX) gave *p*-chlorobenzenesulphinic acid and the nitro-disulphide, whilst *p*-tolyl disulphoxide and *p*-chlorophenyl disulphoxide gave the corresponding sulphinic acids and disulphides or mercaptans. These results are similar to those obtained by Gutmann (*Ber.*, 1914, **47**, 635) on reduction with sodium arsenite. In the cases of disulphoxides containing similar aromatic groups, this result does not enable a decision to be made in favour of either structure, for both permit the formation of a sulphinic acid by hydrolytic fission,

$$R{\cdot}SO{\cdot}SO{\cdot}R \longrightarrow R{\cdot}SO_2H + R{\cdot}S{\cdot}OH \longleftarrow R{\cdot}SO_2{\cdot}SR$$

whilst the disulphide would result from reduction of the less stable sulphenic acids. Turning to the case of a disulphoxide containing different aromatic groups, a distinction between the requirements of either structure is found. On the basis of the symmetrical arrangement, the formation of two sulphinic acids may be expected, for there is no reason to suppose that hydrolysis will take place in one direction only when R^1 and R^2 are of similar character :

$$R^1S{\cdot}OH + R^2{\cdot}SO_2H \longleftarrow R^1{\cdot}SO{\cdot}SO{\cdot}R^2 \longrightarrow R^1{\cdot}SO_2H + R^2{\cdot}S{\cdot}OH.$$

On the other hand, according to the thiosulphonate structure only one sulphinic acid should be formed :

$$2R^1{\cdot}SO_2{\cdot}S{\cdot}R^2 \longrightarrow 2R^1{\cdot}SO_2H + (SR^2)_2$$

The latter condition accords with the result obtained by the reduction of these substances, only one sulphinic acid has been isolated in each case examined. Moreover, it is significant that the sulphinic acid isolated was always the one which had been used as a component in the synthesis, thus nitrophenyl toluenethiolsulphonate (VIII) yielded *p*-toluenesulphinic acid and *o*-nitrophenyl disulphide,

$$2C_7H_7{\cdot}SO_2{\cdot}S{\cdot}C_6H_4{\cdot}NO_2 \longrightarrow 2C_7H_7{\cdot}SO_2H + (NO_2{\cdot}C_6H_4{\cdot}S{\cdot})_2,$$

and nitrophenyl chlorobenzenethiolsulphonate (IX) gave *p*-chlorobenzenesulphinic acid and the nitro-disulphide :

$$2C_6H_4Cl{\cdot}SO_2{\cdot}S{\cdot}C_6H_4{\cdot}NO_2 \longrightarrow 2C_6H_4Cl{\cdot}SO_2H + (NO_2{\cdot}C_6H_4{\cdot}S{\cdot})_2.$$

The action of mercaptans with these disulphoxides is closely analogous (compare Smiles and Gibson, *loc. cit.*). *o*-Nitrophenyl mercaptan yields in both cases the *o*-nitrophenyl disulphide and the correponding sulphinic acid :

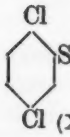
$$\begin{matrix} C_7H_7{\cdot}SO_2{\cdot}S{\cdot}C_6H_4{\cdot}NO_2 \\ H{\cdot}S{\cdot}C_6H_4{\cdot}NO_2 \end{matrix} \qquad \begin{matrix} C_6H_4Cl{\cdot}SO_2{\cdot}S{\cdot}C_6H_4{\cdot}NO_2 \\ H{\cdot}S{\cdot}C_6H_4{\cdot}NO_2 \end{matrix}$$

The information gained from this extended study of the reduction of the disulphoxides therefore clearly favours the unsymmetrical structure. Taking a general review of the characteristic reactions of the disulphoxides, it is seen that all yield the sulphinic acid and a product which contains the thioaryl group; these substances result from the action of zinc dust, magnesium alkyl halides, potassium sulphide, mercaptans, and of arsenite and other mild reducing agents. The majority of these reactions indicate an unsymmetrical structure, a few are ambiguous in their import, whilst none insists on the symmetrical arrangement.

To establish more firmly the unsymmetrical constitution, disulphoxides each containing different aromatic groups have been synthesised by alternate methods. In the first series of experiments it seemed desirable to arrange that the aromatic groups R^1 and R^2 should differ by the nature of the substituents present and not merely by the position of these. The more stable of the known aromatic sulphur chlorides contain the nitro-group and it was obvious to choose one of these as a component of one method of synthesis, but the chief difficulty lay in obtaining a sulphur chloride of sufficient stability without this group for use in the alternate

process. This was overcome by the preparation of 2 : 5-dichlorophenylsulphur chloride (X) from the corresponding disulphide and chlorine.

From 2-nitrophenylsulphur chloride and silver 2 : 5-dichlorobenzenesulphinate a *disulphoxide* (XIa) of m. p. 142° was obtained, whilst from 2 : 5-dichlorobenzenesulphur chloride and silver 2-nitrobenzenesulphinate an isomeric compound (XIIa) melting at 129° was prepared. These substances differ not only in their physical properties but also in their chemical behaviour. When 2-nitrophenyl 2 : 5-dichlorobenzenethiolsulphonate (XIa) is treated with 2-nitrophenyl mercaptan, the dichlorobenzenesulphinic acid and *o*-nitrophenyl disulphide are formed (XI), whilst the action of the same mercaptan with 2 : 5-dichlorophenyl 2-nitrobenzenethiolsulphonate (XIIa) yields *o*-nitrobenzenesulphinic acid and a mixture of the two possible disulphides (compare Smiles and Gibson, *loc. cit.*).



(X).

(*a*) $C_6H_3Cl_2\cdot SO_2\cdot S\cdot C_6H_4\cdot NO_2$
$HS\cdot C_6H_4\cdot NO_2$
(XI.)

(*a*) $C_6H_3Cl_2\cdot S\cdot SO_2\cdot C_6H_4\cdot NO_2$
$C_6H_3Cl_2\cdot SH$
(XII.)

The action of 2 : 5-dichlorophenyl mercaptan with the latter disulphoxide yielded (XII) the nitrosulphinic acid and the tetrachloro-disulphide. Mild reduction of these disulphoxides gave analogous results; these are collected on a subsequent page.

A second series of experiments was made with material in which the groups R^1 and R^2 were closely similar, for it was thought that such conditions would be favourable to intramolecular change—if indeed this were possible—of one thiolsulphonate to the other or of the thiolsulphonate to the true α-disulphoxide structure, the latter change having been suggested by previous workers (Hinsberg, *loc. cit.*; Fries, *loc. cit.*). The materials chosen were the 2 : 5-dichloro- and 2 : 5-dibromo-phenyl derivatives. Thus 2 : 5-dichlorophenylsulphur chloride (X) and silver 2 : 5-dibromobenzenesulphinate furnished 2 : 5-dichlorophenyl 2 : 5-dibromobenzenethiolsulphonate (XIIIa), which melted at 119° even after being heated to 150° and cooled.

On treatment with 2 : 5-dichlorophenyl mercaptan the tetrachloro-disulphide and 2 : 5-dibromobenzenesulphinic acid were formed (XIII), the structure indicated by synthesis being thus confirmed.

(*a*) $C_6H_3Cl_2\cdot S\cdot SO_2\cdot C_6H_3Br_2$
$C_6H_3Cl_2\cdot SH$
(XIII.)

(*a*) $C_6H_3Cl_2\cdot SO_2\cdot S\cdot C_6H_3Br_2$
$HS\cdot C_6H_3Br_2$
(XIV.)

The isomeric 2 : 5-dibromophenyl 2 : 5-dichlorobenzenethiolsulphonate (XIVa), prepared in a similar manner, melted at 125° and with 2 : 5-dibromophenyl mercaptan yielded the tetrabromodisulphide and 2 : 5-dichlorobenzenesulphinic acid (XIV).

In summarising the results of these experiments, it is claimed that an unsymmetrical structure must be assigned to the disulphoxides. Two unsymmetrical formulæ have been advocated, the thiolsulphonate and the anhydride arrangements (II and III); there is ample reason for discarding the latter (Fries, *loc. cit.*), whilst the former accords very closely with all the facts since discovered.

Experimental.

The disulphoxides were obtained, those containing similar aromatic groups from the sulphinic acids by the usual method, and those with dissimilar groups by the reaction of a silver sulphinate with the requisite sulphur chloride as follows. A solution of the sulphur halide in dry ether was shaken at the ordinary temperature or boiled with an excess of the silver sulphinate until all the sulphur halide had disappeared, the treatment being adapted to the reactivity of the materials and the stability of the sulphur halide used. Generally, the disulphoxide separated as the reaction proceeded; when this was complete, the solid material was collected and the disulphoxide was extracted from it with a suitable solvent. In the majority of the cases studied, the yields were good. The following substances were obtained by this method from the stated components.

2-*Nitrophenyl* 4-*toluenethiolsulphonate*, $O_2N\cdot C_6H_4\cdot S\cdot SO_2\cdot C_6H_4Me$, from *o*-nitrophenylsulphur chloride and silver toluenesulphinate, formed colourless prisms, m. p. 97°, soluble in the usual organic solvents (Found : S = 20·7; C = 50·0; H = 3·7. $C_{13}H_{11}O_4NS_2$ requires S = 20·69; C = 50·55; H = 3·58 %). The alcoholic solution of this substance became blue on addition of aqueous sodium hydroxide.

2-*Nitrophenyl* 4-*chlorobenzenethiolsulphonate*,

$$O_2N\cdot C_6H_4\cdot S\cdot SO_2\cdot C_6H_4Cl,$$

from *o*-nitrophenylsulphur chloride and silver *p*-chlorobenzenesulphinate, formed colourless prisms, m. p. 123°, soluble in the usual organic media (Found : S = 19·6; Cl = 10·5; C = 43·3; H = 2·66. $C_{12}H_8O_4NClS_2$ requires S = 19·42; Cl = 10·74; C = 43·68; H = 2·44 %).

2-*Nitrophenyl* 2 : 5-*dichlorobenzenethiolsulphonate*,

$$O_2N\cdot C_6H_4\cdot S\cdot SO_2\cdot C_6H_3Cl_2,$$

from *o*-nitrophenylsulphur chloride and silver 2 : 5-dichlorobenzenesulphinate, melted at 142° and was sparingly soluble in common

solvents (Found : Cl = 19·4; S = 17·6. $C_{12}H_7O_4NCl_2S_2$ requires Cl = 19·47; S = 17·61 %). Like the foregoing disulphoxides, this substance gave a deep blue solution with alcoholic sodium hydroxide.

2 : 5-*Dichlorophenyl* 2-*nitrobenzenethiolsulphonate*,

$$C_6H_3Cl_2\cdot S\cdot SO_2\cdot C_6H_4\cdot NO_2,$$

from silver *o*-nitrobenzenesulphinate and 2 : 5-dichlorophenylsulphur chloride, separated from hot alcohol in colourless needles, m. p. 129° (Found : S = 17·6; Cl = 19·6. $C_{12}H_7O_4NCl_2S_2$ requires S = 17·6; Cl = 19·47 %); aqueous sodium hydroxide added to the alcoholic solution did not give the characteristic blue colour. A mixture of the two isomeric substances in approximately equal amounts melted indefinitely between 88—95°.

2 : 5-*Dichlorophenyl* 2 : 5-*dibromobenzenethiolsulphonate*,

$$C_6H_3Cl_2\cdot S\cdot SO_2\cdot C_6H_3Br_2,$$

from 2 : 5-dichlorophenylsulphur chloride and silver 2 : 5-dibromobenzenesulphinate, separated from alcohol in colourless needles, m. p. 119° (Found : S = 13·8; Cl + Br = 48·3. $C_{12}H_6O_2Cl_2Br_2S_2$ requires S = 13·45; Cl + Br = 48·38 %).

2 : 5-*Dibromophenyl* 2 : 5-*dichlorobenzenethiolsulphonate*,

$$C_6H_3Br_2\cdot S\cdot SO_2\cdot C_6H_3Cl_2,$$

from silver 2 : 5-dichlorobenzenesulphinate and 2 : 5-dibromophenylsulphur bromide, separated from hot alcohol in colourless prisms, m. p. 125.° This melting point remained unaltered after a sample had been fused and cooled. The substance is less soluble than the isomeric disulphoxide, and a mixture of the two in approximately equal amounts melted indefinitely at 110—114° (Found : S = 13·4; Cl + Br = 48·5. $C_{12}H_6O_2Cl_2Br_2S_2$ requires S = 13·45; Cl + Br = 48·38 %).

2 : 5-*Dichlorophenylsulphur chloride*, $C_6H_3Cl_2\cdot SCl$, was prepared by saturating a concentrated solution of the corresponding disulphide in dry carbon tetrachloride with chlorine. The residue obtained after the solvent had been evaporated was kept under diminished pressure, when it solidified. The product was purified by crystallisation from ice-cold ether, when the substance was obtained in golden-yellow needles, m. p. 32—33° (Found : Cl = 49·8; S = 14·9. $C_6H_3Cl_3S$ requires Cl = 49·8; S = 15·03 %). The substance was very soluble in organic media; dilute aqueous sodium hydroxide gave the corresponding disulphide and alkali sulphinate. The 2 : 5-dibromophenylsulphur bromide was obtained by a similar process as a yellow, crystalline material, but owing to its instability attempts to isolate it in a pure condition for analysis were unsuccessful, some loss of bromine occurring with formation of the disulphide.

Behaviour of Disulphoxides with Methyl and Phenyl Magnesium Halides.—A dilute solution of the disulphoxide in ether was added to a cooled solution of the magnesium compound (1 mol.) in the

Disulphoxide.	Magnesium derivative.	Sulphinic acid %.	Other substances observed.
Diphenyl	Methyl	63	Ph·S·Me; PhS·SPh.
Diphenyl	Phenyl	70	Ph·S·Ph; PhS·SPh; Ph·Ph.
Di-*p*-tolyl	Methyl	87	C_7H_7·S·Me; C_7H_7·S·S·C_7H_7.
Di-*p*-tolyl	Phenyl	76	C_7H_7·S·Ph; (C_7H_7·S·)$_2$ and Ph·Ph.
Di-*p*-chlorophenyl	Methyl	90	C_6H_4Cl·S·Me; (C_6H_4Cl·S·)$_2$.
2 : 5 : 2′ : 5′-Tetrachlorodiphenyl	,,	82	
4 : 4′-Dimethoxytolyl 3 : 3′-disulphoxide	,,	68	MeO·C_6H_4·S·Me; and disulphide.

same solvent. The mixture was kept for 12 hours before treatment with water. Sufficient aqueous sodium thiosulphate was then added to remove free iodine, if this were present, and finally excess of dilute sulphuric acid. The sulphinic acid was extracted from the ethereal solution with dilute alkali, the substances remaining being separately examined. A summary of the results is given in the foregoing table. The third column shows the approximate percentages in which the sulphinic acids were isolated. These substances were identified by comparison with authentic samples and by conversion to the methylsulphones, which were similarly compared. The latter have been previously described in literature with the exception of the following.

4-*Chlorophenylmethylsulphone*, $C_6H_4Cl·SO_2·CH_3$, colourless needles, m. p. 96°, was obtained by oxidation of the sulphide and by methylation of the sodium sulphinate with methyl sulphate (Found: Cl = 18·7; S = 16·6. $C_7H_7O_2ClS$ requires Cl = 18·58; S = 16·8 %).

2 : 5-*Dichlorophenylmethylsulphone*, $C_6H_3Cl_2·SO_2·CH_3$, prepared in a similar manner, separated from hot water in needles, m. p. 88° (Found: S = 14·0. $C_7H_6O_2Cl_2S$ requires S = 14·24 %). The identification of sulphides was generally effected by oxidation to the sulphones.

Action of Mercaptans with Disulphoxides.—The method of operation was similar to that already described (Smiles and Gibson, *loc. cit.*), molecular proportions of the reagents being taken in alcohol. The results are collected in the following table; the third and fourth columns, respectively, show the sulphinic acid and the disulphide which were isolated from the interaction of the stated disulphoxide and mercaptan. The yields of these products were generally of the order of 80% of theory and higher when the sparingly soluble

2 : 2′-dinitrodiphenyl disulphide was dealt with. The numerals in the first column refer to numbered formulæ.

Disulphoxide.	Mercaptan.	Sulphinic acid.	Disulphide.
2-Nitrophenyl 4-toluenethiolsulphonate (VIII)	2-Nitrophenyl	4-Toluene-	Di-*o*-nitrophenyl
2-Nitrophenyl 4-chlorobenzenethiolsulphonate (IX)	„	4-Chlorobenzene-	„
2-Nitrophenyl 2 : 5-dichlorobenzenethiolsulphonate (XI)	„	2 : 5-Dichlorobenzene-	„
2 : 5-Dichlorophenyl 2-nitrobenzenethiolsulphonate (XII)	2 : 5-Dichlorophenyl	2-Nitrobenzene-	2 : 5 : 2′ : 5′-Tetrachlorodiphenyl
2 : 5-Dichlorophenyl 2-nitrobenzenethiolsulphonate (XII)	2-Nitrophenyl	„	A mixture: not separated
2 : 5-Dichlorophenyl 2 : 5-dibromobenzenethiolsulphonate (XIII)	2 : 5-Dichlorophenyl	2 : 5-Dibromobenzene-	2 : 5 : 2′ : 5′-Tetrachlorodiphenyl
2 : 5-Dibromophenyl 2 : 5-dichlorobenzenethiolsulphonate (XIV)	2 : 5-Dibromophenyl	2 : 5-Dichlorobenzene-	2 : 5 : 2′ : 5′-Tetrabromodiphenyl

Reduction of Disulphoxides.—Three methods of reduction were employed. In cases 1, 2, and 3 of the following table, where complete reduction with hydrogen iodide was required, the conditions devised by Hinsberg (*Ber.*, 1908, **41**, 4295) were used. Milder reduction with this reagent was effected as follows. About 2 g. of the disulphoxide, 3—4 c.c. of glacial acetic acid, and a few c.c. of a saturated solution of sodium bisulphite containing ten drops of hydriodic acid (*d* 1·9) were constantly shaken with 50—100 c.c. of light petroleum for about ½ hour, the necessary time varying somewhat according to the disulphoxide taken. Then aqueous sodium carbonate was added until the whole was alkaline. In cases where the dinitro-disulphide was formed, this separated almost completely from the liquid. The solid material was collected, the petroleum and the aqueous portion of the liquid being separately examined. The sulphinic acid was isolated from the aqueous portion and the disulphide from the solid or the petroleum. Examples of this type of reduction are given in Nos. 4, 5, 6, and 7 of the table. Reduction with sodium hyposulphite was conducted by shaking the disulph-

oxide with a slight excess of a 3—4 % aqueous solution of the reagent to which about 1/10th of its volume of alcohol had been added, the mixture being kept alkaline by the addition of sodium carbonate. The disulphide formed was isolated by solution in ether, whilst the sulphinic acid and mercaptan were obtained from the aqueous portion. When mercaptan was present, this was separated from the sulphinic acid as disulphide by treating the solution of sodium salts with a current of air. Examples are shown in Nos. 8, 9, and 10 of the table.

	Disulphoxide.	Products isolated.
1.	2-Nitrophenyl 4-toluenethiolsulphonate	2 : 2′-Dinitrodiphenyl disulphide
2.	2-Nitrophenyl 4-chlorobenzenethiolsulphonate	2 : 2′-Dinitrodiphenyl disulphide and 4 : 4′-dichlorodiphenyl disulphide
3.	2 : 5-Dichlorophenyl 2-nitrobenzenethiolsulphonate	A mixture of disulphides; not separated
4.	2-Nitrophenyl 4-toluenethiolsulphonate	4-Toluenesulphinic acid and 2 : 2′-dinitrodiphenyl disulphide
5.	2-Nitrophenyl 4-chlorobenzenethiolsulphonate	4-Chlorobenzenesulphinic acid and 2 : 2′-dinitrodiphenyl disulphide
6.	Di-4-chlorophenyl disulphoxide	4-Chlorobenzenesulphinic acid and 4 : 4′-dichlorodiphenyl disulphide
7.	2-Nitrophenyl 2 : 5-dichlorobenzenethiolsulphonate	2 : 5-Dichlorobenzenesulphinic acid and 2 : 2′-dinitrodiphenyl disulphide
8.	Di-*p*-tolyl disulphoxide	*p*-Toluenesulphinic acid and *p*-tolyl mercaptan
9.	2 : 5-Dichlorophenyl 2-nitrobenzenethiolsulphonate	2-Nitrobenzenesulphinic acid and 2 : 5 : 2′ : 5′-tetrachlorodiphenyl disulphide
10.	2-Nitrophenyl 2 : 5-dichlorobenzenethiolsulphonate	2 : 5-Dichlorobenzenesulphinic acid, 2-nitrothiophenol, and the disulphide

In conclusion, we desire to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in this work. Our thanks are also due to Mr. W. E. Wright for the derivatives of 2 : 5-dibromophenyl mercaptan used in these experiments.

KING'S COLLEGE, LONDON. [*Received, November* 11*th*, 1924.]

XXXIX.—*Resolution of Chlorosulphoacetic Acid into its Optically Active Components.*

By HILMAR JOHANNES BACKER and WILHELM GERARD BURGERS.

CHLOROSULPHOACETIC acid, $SO_3H{\cdot}CHCl{\cdot}CO_2H$, one of the simplest compounds with an asymmetric carbon atom, has hitherto resisted all attempts at optical resolution. Porcher stated (*Bull. Soc. chim.*, 1902, [iii], 27, 438) that resolution is possible, but Pope and

Read, repeating his experiments, did not confirm his results and were led " to dismiss them as not in accordance with experiment " (J., 1908, **93**, 794; 1914, **105**, 811).

We have resolved the racemic acid by a method which apparently had not previously been applied to such purposes, namely, by slow crystallisation of alkaloidal salts in the cold.

After a preliminary examination of their solubility, the alkaloid salts of chlorosulphoacetic acid were prepared by treating the sodium salt at room temperature with a soluble salt of the alkaloid in such dilution that crystallisation of the product did not start at once and only a small part was subsequently deposited. Since the solubility of the alkaloid salts was so small that the effect of the active chlorosulphoacetic acid on the rotation was inappreciable, the sodium and ammonium salts were examined.

For purification, the same " cold crystallisation " was used. The alkaloid salt was therefore converted at 0° into the ammonium salt by means of the theoretical quantity of dilute ammonia, the alkaloid was filtered off, and the solution of the ammonium salt was mixed with the alkaloid (as acetate) in such concentration that again only a part of the alkaloid salt crystallised. By means of yohimbine a dextrorotatory ammonium salt was obtained, and an acid of nearly twice the rotation. *l*-Strychnine gave the dextrorotatory acid, whilst *d*-cinchonine furnished the lævo-component, so that the small rotation we first obtained could not be ascribed to the presence of traces of the alkaloids. The highest, constant value of the molecular rotation was for the acid $[M]_D = \pm 39°$ and for the neutral ammonium salt $[M]_D = \pm 20°$.

The acids and their salts gradually racemise in solution at room temperature. Bases accelerate racemisation of the salts. On evaporation, the solutions lose their activity completely. These active acids, therefore, are more stable than fluorochlorobromoacetic acid, which shows activity only in its alkaloidal salts (Swarts, *Bull. roy. Belg.*, 1896, [iii], **31**, 25), but they do not attain the high stability of chloroiodomethanesulphonic acid, which is not racemised by any of the usual methods (Pope and Read, *loc. cit.*).*

Experimental.

Preparation of Chlorosulphoacetic Acid.—The method used for the preparation of other sulphocarboxylic acids (*Rec. trav. chim.*, 1920, **39**, 694; 1924, **43**, 297) gives a good yield and a pure product.

* This research is being continued and the method will be applied to other resolutions. The present results are published because of the departure of Mr. Burgers.—H. J. B.

To 94 g. (1 mol.) of freshly distilled chloroacetic acid, cooled with ice, are gradually added 80 g. (1 mol.) of sulphur trioxide with constant shaking. A viscous, nearly colourless syrup of the mixed anhydride of sulphuric and chloroacetic acids is formed (Found by titration after decomposition with water: equiv. = 57. $CH_2Cl{\cdot}CO{\cdot}O{\cdot}SO_3H$, decomposed by water into $CH_2Cl{\cdot}CO_2H + H_2SO_4$, requires a mean equivalent weight of $174{\cdot}5/3 = 58{\cdot}2$). The anhydride is converted into the sulphonic acid by warming: $CH_2Cl{\cdot}CO{\cdot}O{\cdot}SO_3H \longrightarrow SO_3H{\cdot}CHCl{\cdot}CO_2H$. At 70° the external heating is discontinued; the heat of reaction causes the temperature to rise to about 140°, the liquid becoming coloured towards 100° and a feeble evolution of gas (CO_2 and SO_2) setting in. The product is a brown syrup, consisting mainly of chlorosulphoacetic acid (Found: equiv. = 84. Calc. equiv. = $174{\cdot}5/2 = 87{\cdot}2$). When kept over-night, the acid may crystallise.

A solution of the syrup or crystallised mass in 5 litres of water is treated with barium carbonate in excess (200 g.). The filtrate, evaporated to 250 c.c. and cooled, deposits 270 g. of pure crystalline barium chlorosulphoacetate (yield more than 80%) (Found: Ba = 41·83, 41·84. Calc., Ba = 41·89%). On concentration, the mother-liquor gives, as in Andreasch's preparation (*Monatsh.*, 1886, **7**, 158), crystals of barium chloromethanedisulphonate (about 15 g.) (Found: $H_2O = 17{\cdot}37$; Ba = 32·56, 32·54. Calc. for $CHO_6ClS_2Ba,4H_2O$, $H_2O = 17{\cdot}24$; Ba = 32·86%).

Chlorosulphoacetic acid was prepared by shaking its barium salt mechanically for 1 hour with the calculated quantity of 2*N*-sulphuric acid. The filtrate, which was free from sulphuric acid and barium, was concentrated first by distillation under reduced pressure, then in a desiccator over sulphuric acid, and finally over phosphorus pentoxide until crystallisation set in.

Chlorosulphoacetic acid forms very hygroscopic crystals containing $1H_2O$ (Found: $M = 191{\cdot}8$. Calc. for $C_2H_3O_5ClS,H_2O$, $M = 192{\cdot}56$). The melting point, determined in an apparatus for hygroscopic substances (*Chem. Weekblad*, 1919, **16**, 1564), was 83°.

Normal Alkaloidal Salts.—The normal salts of chlorosulphoacetic acid with various alkaloids were prepared either by dissolving the bases in the equivalent quantity of the acid, or by double decomposition from sodium chlorosulphoacetate with a soluble salt, usually the acetate or phosphate, of the alkaloid. The salts, all of which were obtained in the crystalline state,* were titrated with sodium hydroxide in presence of phenolphthalein or thymolphthalein.

* Pope and Read state that the quinine and cinchonine salts were not obtained crystalline. Their strychnine salt contained $1H_2O$.

The normal *quinine* salt forms a felted mass of small needles containing $4H_2O$ (Found: $H_2O = 8{\cdot}03$; $M = 894$.

$C_2H_3O_5ClS,2C_{20}H_{24}O_2N_2,4H_2O$

requires $H_2O = 8{\cdot}05\%$; $M = 895{\cdot}0$).

The normal *cinchonine* salt crystallises with $1H_2O$ in silky needles, concentrically arranged in dense globules (Found: $H_2O = 2{\cdot}36$; $M = 780$. $C_2H_3O_5ClS,2C_{19}H_{22}ON_2,H_2O$ requires $H_2O = 2{\cdot}31\%$; $M = 780{\cdot}9$).

The normal *strychnine* salt, when crystallised from a dilute solution, forms needles, about $\frac{1}{4}$ inch long, containing $3H_2O$ (Found: $H_2O = 6{\cdot}08, 6{\cdot}15$; $M = 896{\cdot}7, 897{\cdot}2, 895{\cdot}8$.

$C_2H_3O_5ClS,2C_{21}H_{22}O_2N_2,3H_2O$

requires $H_2O = 6{\cdot}03\%$; $M = 897$).

d-*Chlorosulphoacetic Acid.*—Sodium chlorosulphoacetate (0·05 mol.) in 1150 c.c. of water was treated with 33·4 g. (0·1 mol.) of strychnine dissolved in the same volume of water containing 11 g. of acetic acid. Slender needles began to separate within 1 hour, and after 10 hours, at 20°, 9 g. of strychnine salt were collected, corresponding to 20% of the quantity formed (44·8 g.).

For polarimetric examination, weighed quantities of the strychnine salt (0·5—2 g.) were shaken at 0° with the theoretical quantity of dilute ammonia, the volume was brought to 20 c.c., and the solution of the ammonium salt, after being extracted four times with half its volume of chloroform, was examined by means of a polarimeter (Schmidt and Haensch) with monochromator. In some cases, the concentration of the ammonium salt was verified by evaporation of the solution. The rotatory power was measured for $\lambda = 589\ \mu\mu$ (D) and for two arbitrary wave-lengths in the green ($\lambda = 533\ \mu\mu$) and blue ($\lambda = 494\ \mu\mu$). The ammonium salt, prepared from the strychnine salt mentioned above, gave the following figures: Concentration 0·00480 g.-mol. in 100 c.c.; $l = 2$; $\alpha_D = +0{\cdot}18°$; $[M]_D = +18{\cdot}7°$.

For recrystallisation, 4·48 g. (0·005 mol.) of the active strychnine salt were decomposed by ammonia. The separated strychnine was dissolved in dilute acetic acid and added to the solution of the ammonium salt. The total volume being 230 c.c., the concentration was the same as above. 1·3 Grams, or nearly 30%, separated. Rotation of the ammonium salt: Conc. 0·01115 g.-mol. in 100 c.c.; $l = 2$; $\alpha_D = +0{\cdot}45°$, $\alpha_{533} = +0{\cdot}58°$, $\alpha_{494} = +0{\cdot}74°$; $[M]_D = +20{\cdot}2°$, $[M]_{533} = +26{\cdot}0°$, $[M]_{494} = +33{\cdot}2°$. Conc. 0·00560 g.-mol. in 100 c.c.; $l = 2$; $\alpha_D = +0{\cdot}23°$, $\alpha_{533} = +0{\cdot}30°$, $\alpha_{494} = +0{\cdot}37°$; $[M]_D = +20{\cdot}5°$, $[M]_{533} = +26{\cdot}8°$, $[M]_{494} = +33{\cdot}0°$.

Addition of sulphuric acid to liberate the acid (2 mols. for 1 mol. of ammonium salt) increased the rotatory power, but this did not change

further on addition of more sulphuric acid. Rotation of the free acid: Conc. 0·005 g.-mol. in 100 c.c.; $l = 2$; $\alpha_D = +0{\cdot}40°$, $\alpha_{533} = +0{\cdot}52°$, $\alpha_{494} = +0{\cdot}62°$; $[M]_D = +40°$, $[M]_{533} = +52°$, $[M]_{494} = +62°$.

l-*Chlorosulphoacetic Acid.*—Sodium chlorosulphoacetate (0·05 mol.) was mixed with 30 g. (0·1 mol.) of cinchonine dissolved in water containing 9 g. of acetic acid. The total volume was 1150 c.c. After 2 days, 5·5 g. of the cinchonine salt, or 14% of the total amount (39 g.), had separated.

The product was decomposed with ammonia like the strychnine salt, the only difference being that the alkaloid was filtered off before extraction of the solution with chloroform. Rotation of the ammonium salt: Conc. 0·00278 g.-mol. in 100 c.c.; $l = 2$; $\alpha_D = -0{\cdot}08°$; $[M]_D = -14{\cdot}4°$.

The active cinchonine salt (3·9 g.; 0·005 mol.) was recrystallised in the same way as the strychnine salt. From 115 c.c., the same concentration as above, there separated 0·95 g. or 25%. Rotatory power of the ammonium salt: Conc. 0·00324 g.-mol. in 100 c.c.; $l = 2$; $\alpha_D = -0{\cdot}12°$, $\alpha_{533} = -0{\cdot}17°$, $\alpha_{494} = -0{\cdot}23°$; $[M]_D = -18{\cdot}5°$, $[M]_{533} = -26{\cdot}2°$, $[M]_{494} = -35{\cdot}5°$.

The acid liberated by an excess of sulphuric acid gave the figures: Conc. 0·00305 g.-mol. in 100 c.c.; $\alpha_D = -0{\cdot}23°$, $\alpha_{533} = -0{\cdot}29°$, $\alpha_{494} = -0{\cdot}38°$; $[M]_D = -37{\cdot}7°$, $[M]_{533} = -47{\cdot}5°$, $[M]_{494} = -62{\cdot}3°$.

Thus the mean values for the rotatory power are:

Chlorosulphoacetic acid: $[M]_D = \pm 39°$, $[M]_{533} = \pm 50°$, $[M]_{494} = \pm 62°$.

Neutral ammonium salt: $[M]_D = \pm 20°$, $[M]_{533} = \pm 26°$, $[M]_{494} = \pm 34°$.

Racemisation.

The rotation of a neutral solution of the *d*-ammonium salt containing 0·1 mol. per litre had fallen in a fortnight to half its value. The rotation of a solution containing 0·05 mol. of the *d*-acid per litre and an excess of sulphuric acid diminished in 10 days by one-fourth.

A solution of 0·05 mol. of the ammonium salt per litre containing 0·1 mol. of free ammonia had lost one-third of its rotatory power within 24 hours. Examined a week later, it was inactive.

The *d*-acid and the *d*-ammonium salt, each in a solution containing 0·05 mol. per litre, were rapidly heated, boiled for 1 minute, and immediately cooled. Their rotatory powers had decreased by about 5%. The same solutions, evaporated on a water-bath and diluted to the original volume, racemised completely.

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XL.—*The Rotatory Dispersive Power of Organic Compounds. Part XIV. Simple Dispersion in* 1-*Methylcyclohexylidene*-4-*acetic Acid.*

By Evan Matthew Richards and Thomas Martin Lowry.

Special interest attaches to the rotatory dispersion of centro-asymmetric compounds, which (according to the ordinary definition) contain no asymmetric atom. Through the kindness of Professor Pope we have recently had the opportunity of studying from this point of view his own specimens (compare J., 1909, **95**, 1789) of the *d*- and *l*-forms of the well-known acid,

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>\!C\!=\!C\!<\!\begin{matrix}H\\CO\cdot OH.\end{matrix}$$

On Professor Pope's recommendation, the measurements were made with solutions in methylal. The volatility of this solvent made it necessary to express the results in the form of dispersion-ratios, instead of by means of specific or molecular rotations, since the solutions were originally cloudy and their concentrations were altered appreciably by filtration; but we had the very great advantage of being able (except in the photographic region) to read a dextro against a lævo solution, under precisely similar conditions, without being compelled to make use of zero-readings. In these circumstances, a very satisfactory agreement was obtained between the results recorded in two complete series of independent readings.

The data are set out in Table I, together with the corresponding dispersion-ratios calculated from the equation $\alpha/\alpha_{5461} = 0{\cdot}2422/(\lambda^2 - 0{\cdot}056)$. Since the value of α_{5461} was about 20° for the visual and 10° for the photographic observations, an error of 0·001 in the dispersion-ratios corresponds with an error of 0·02° in the visual readings, and of 0·01° in the photographic readings.

The largest visual error was therefore about 0·2° (for a difficult dark-blue line) and the largest photographic error about 0·3°. The average error in the visual ratios is 0·003, and in the photographic ratios 0·02; the negative and positive errors are, moreover, distributed in small groups, and afford no evidence of systematic deviations from the formula, such as were observed in the case of octyl oxalate.

The data can be expressed, over the range of wave-lengths covered by our observations and up to the existing limits of experimental accuracy, by one term of Drude's equation. Moreover, since an exposure of more than an hour was required to give the last photographic reading, it is clear that the measurements had been carried right up to the limit of the region of transparency, within

TABLE I.

Dispersion-ratios of 1-Methyl*cyclo*hexylidene-4-acetic Acid in Methylal (about 6 gms. per 100 c.c.) at 20°.* Mol. wt. 154·17.

$a/a_{5461} = 0{\cdot}2422/(\lambda^2 - 0{\cdot}056)$.

Line.		Sum of d and l rotations. First series.	Sum of d and l rotations. Second series.	Dispersion-ratios a/a_{5461}. First series.	Dispersion-ratios a/a_{5461}. Second series.	Mean.	Calc.	Diff.
Li	6708	12·81	11·00	0·611	0·602	0·607	0·615	−0·008
Cd	6438	14·20	12·31	0·678	0·674	0·676	0·676	±
Zn	6362	14·53	12·56	0·694	0·688	0·691	0·694	−0·003
Na	5893	17·41	15·20	0·831	0·832	0·832	0·832	±
Cu	5782	18·24	15·91	0·870	0·871	0·871	0·870	+0·001
Hg	5780	18·23	15·88	0·870	0·870	0·870	0·871	−0·001
Cu	5700	18·82	16·45	0·898	0·901	0·900	0·901	−0·001
Hg	5461	20·95	18·26	1·000	1·000	1·000	1·000	±
Cu	5218	23·48	20·47	1·121	1·121	1·121	1·120	+0·001
Cu	5153	24·29	21·19	1·160	1·160	1·160	1·156	+0·004
Cu	5106	24·89	21·64	1·188	1·185	1·187	1·183	+0·004
Cd	5086	25·19	21·85	1·202	1·196	1·199	1·195	+0·004
Zn	4811	28·87	—	1·378	—	1·378	1·381	−0·003
Cd	4800	29·14	25·32	1·391	1·386	1·389	1·389	±
Zn	4722	30·48	26·60	1·455	1·456	1·456	1·450	+0·006
Zn	4680	31·05	27·18	1·482	1·488	1·485	1·486	−0·001
Cd	4678	31·49	27·23	1·503	1·491	1·497	1·487	+0·010
Hg	4358	37·92	32·96	1·810	1·805	1·808	1·808	±

Photographic Series ($a_{5461} = 9{\cdot}54°$).

Line.		Rotation.	Dispersion ratio. Obs.	Dispersion ratio. Calc.	Diff.
Fe	4376	*17·11*	1·79	1·79	±
Fe	4337	*17·36*	1·82	1·83	−0·01
Fe	4308	*17·61*	1·85	1·87	−0·02
Fe	4271	*18·11*	1·90	1·92	−0·02
Fe	4261	*18·36*	1·92	1·93	−0·01
Fe	4236	*18·61*	1·95	1·96	−0·01
Fe	4199	*18·98*	1·99	2·01	−0·02
Fe	4187	*19·23*	2·02	2·03	−0·01
Fe	4144	*20·23*	2·12	2·09	+0·03
Fe	4132	*20·36*	2·13	2·11	+0·02
Fe	4119	*20·61*	2·16	2·13	+0·03
Fe	4072	*21·50*	2·23	2·21	+0·02

* The temperature, 20°, was accidentally omitted from the corresponding tables for octyl alcohol and octyl oxalate in Part XII of this series (J., 1924, 125, 1595, 1596). The opportunity may also be taken of correcting an error in Part XI (*ibid.*, p. 1466, two lines from the bottom), where a shallow minimum "at 5 per cent." should be "at 50 per cent." of ethyl tartrate.

which alone Drude's formula is valid. As any deviations disclosed by pushing the observations beyond this limit would be irrelevant to the present discussion, it appears that the simplicity of the dispersion is not likely to be disproved by direct experimental measurements. Complexity could therefore be established only by the use of indirect tests, such as that described in the previous paper

(p. 2511). In the present instance, however, as in the analogous case of octyl alcohol, this test gives no clear answer to our question, since the characteristic frequency of the dispersion-equation falls in a region in which absorption-bands are very difficult to detect. Thus the dispersion-constant, $\lambda^2 = 0{\cdot}056$, of Pope's acid corresponds to a wave-length, $\lambda = 2364$ Å.U., only a little longer than that of the last strong line in the iron arc spectrum. Direct measurements of the molecular extinction coefficient of the acid in this region (Table II) show, however, that the "general absorption" ($\log \epsilon = 3{\cdot}9$) of the acid at this wave-length is already more than 100 times greater than the maximum selective absorption ($\log \epsilon = 1{\cdot}5$) of camphor and of camphorquinone, at the head of their absorption bands. It was therefore quite impossible to establish the existence of a band of selective absorption at the wave-length indicated. In our opinion, however, a negative result of this character does not provide valid evidence that the dispersion is complex; and until some positive evidence to the contrary is available we propose to describe the dispersion of the compound as simple.

TABLE II.

Molecular Extinction Coefficients.

λ =	2470	2440	2411	2375	2348	2338	2327
$\log \epsilon$ =	3·31	3·61	3·78	3·91	4·01	4·09	4·15

The acid contains only one unsaturated group, namely, the conjugated system $>C{=}CH{-}C{<}^{O}_{OH}$. The characteristic frequency of this is perhaps given by the dispersion-constant of our equation.

We desire to express our thanks to the Department of Scientific and Industrial Research for a maintenance grant to one of the authors (E. M. R.).

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, September 20th*, 1924.]

XLI.—*The Electrical Explosion of Tungsten Wires.*

By HENRY VINCENT AIRD BRISCOE, PERCY LUCOCK ROBINSON, and GEORGE EDWARD STEPHENSON.

THE phenomena accompanying heavy high-tension discharges in thin metallic wires were first studied by Anderson (*Astrophys. J.*, 1920, **51**, 37). Using a large glass plate and tin-foil condenser, he photographed the spectra of the light emitted by the electrical explosion of iron, copper, nickel, and manganin wires and observed

very interesting effects, notably a reversal of many lines, producing an absorption (Fraunhofer) spectrum instead of the bright-line spectrum usually observed. These phenomena are attributable to the momentary attainment of an exceptionally high temperature in the substance of the wire. Observations with a rotating mirror showed that the duration of the flash was less than 10^{-5} second, and Anderson calculated that if the available energy of his condenser, equivalent to about 30 calories, were wholly communicated to the 2 milligrams of wire in this time, the temperature attained would be of the order of 300,000°. The intrinsic brilliancy of the wire at the moment of explosion was found to correspond with a surface temperature of 20,000°. Making liberal allowance for the inherent uncertainty of these estimates, it seems evident that the temperatures attained in such explosions are much higher than can be reached by any other means.

In 1922, Wendt and Irion (*J. Amer. Chem. Soc.*, **44**, 1887) reported the results of experiments on the explosion of fine tungsten wires by Anderson's method. When the explosions were carried out in a vacuum, some gas was formed, and this, subjected to an ordinary high-tension discharge, gave a spectrum in which the yellow helium line, D_3, was consistently observed. When the wires were exploded in an atmosphere of carbon dioxide at ordinary pressure, and the carbon dioxide afterwards absorbed in caustic potash solution, residual gas, averaging 1·42 c.c. per milligram of tungsten, remained. This gas was lost before its spectrum had been investigated. If it consisted wholly or mainly of helium, it was on the average some 25% of the weight of tungsten taken.

These results were so startling, and, if correct, of such profound significance that the experiments here described were undertaken to confirm them.

The essential idea of these experiments is, of course, extremely simple. A fine tungsten wire is supported between heavy electrodes sealed into a glass vessel; this vessel is evacuated, and a heavy discharge is passed from a condenser of large capacity. Thereafter an ordinary high tension-discharge is passed through a capillary side-tube on the bulb, and the emitted light spectroscopically examined. In practice, the experimental difficulties are considerable and arise chiefly in securing the necessary conditions of very high vacuum and very good contact between the wire and the electrodes. Unless both these conditions are fulfilled, the discharge does not pass through the wire, but passes between the electrodes (possibly through the slight conductivity of gas remaining in the bulbs or produced by local heating of the wire) in such a way that the material of the wire is unaffected.

Experimental.

Preparation of Bulbs.—Three containers, of the form shown in Fig. 1, were first constructed from 300 c.c. spherical Durosil bulbs, A, provided with main electrodes, EE, and a supplementary electrode, F, in a small bulb connected with A by a capillary tube, C. While A was still open at the line D, the wire, W, was sprung into place between EE by means of suitable forceps : thereafter the system of tubes, B G H, was sealed on at D. The electrodes, EE, were of heavy molybdenum wire approximately 0·1 inch in diameter : one end of each was drilled and countersunk with fine drills to receive the filament and they were then coated with glass nearly to the ends and sealed into the bulbs as shown in Fig. 3.

Fig. 1.

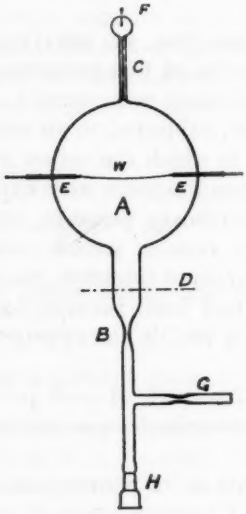
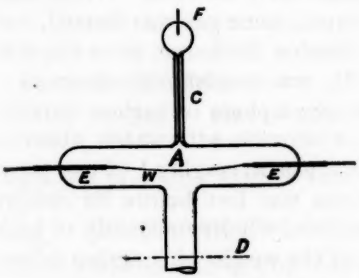


Fig. 2.

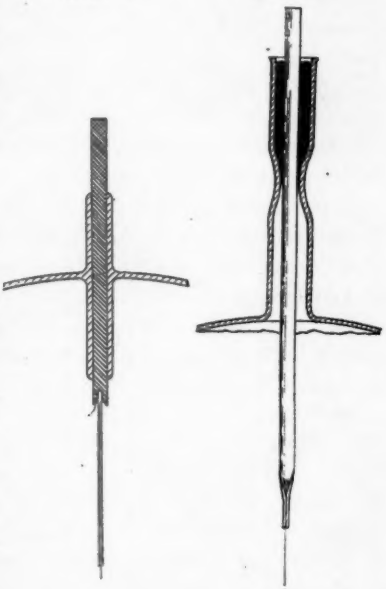


Serious difficulties were encountered in making this apparatus : unless the bulbs were of heavy glass they cracked at the electrode seals and when the seals stood they frequently leaked at pinholes so minute that they could only be detected by a pressure test under water. A T-shaped bulb of about 70 c.c. capacity constructed as in Fig. 2 from Durosil tubing 1″ in diameter proved much more satisfactory.

All attempts to seal heavy tungsten wires into Pyrex glass, as described by Wendt and Irion, failed completely, but, fortunately, it was found that molybdenum sealed fairly well into Durosil glass and could, unlike tungsten, be obtained as drawn wire of the heavy section required to carry the discharge without material loss.

We are indebted to Messrs. Duram Ltd., and to their chemist, Mr. S. C. Radford, who very kindly supplied us with several samples of fine tungsten wire, both hard-drawn and annealed. The annealed wire proved much less springy and easier to handle than the hard-drawn wire and was used throughout: pieces about 4 cm. long were cut from a soft wire 0·035 mm. in diameter. It was quite impossible to spring these wires unsupported between the electrodes as Wendt and Irion stated they had done. With much patience and luck, crystalline filaments from an old drawn-wire lamp could be fitted in this way, but they were so fragile as to be useless in practice. Therefore the wire was threaded through a very fine and light capillary glass tube, bent back outside the tube at both ends, and then the tube and wire were sprung between the electrodes as shown in Figs. 2 and 3.

FIG. 3. FIG. 4.



Bulbs made as described were connected by the mercury-sealed ground glass joint H (Fig. 1) to a large all-glass Töpler pump and McLeod gauge, and, after a preliminary evacuation by a water-pump connected to G, which was then sealed off at the constriction, were further evacuated with the Töpler pump. The first bulb was kept at 300° in an electrically heated air-bath, evacuated to 0·005 mm., and left at 300° over-night. Next morning, the pressure in the bulb was 0·02 mm. This difference appeared to be too large to be accounted for by the release of gases from the glass. The bulb was allowed to cool and each electrode seal was tested, in turn, by coating it with sealing wax and carrying out a series of evacuations. By this means it was established that leakage was occurring in the neighbourhood of the seals. After treating a large surface of the glass with a collodion varnish, a vacuum of 0·001 mm. was maintained over-night. As a further test of this vacuum, an induction coil discharge was passed between the supplementary electrode and one of the main electrodes: there was at first no visible discharge, but after a time, possibly through the release of gas from the wires or accidental breakage of the wax

seals, a noisy visible discharge occurred and set up vibration which dislodged the wire and capillary and so rendered the bulb useless.

The details given above for one case will serve to indicate the difficulties attendant on the use of molybdenum–glass seals: As a result of a series of experiments, another metal–glass seal was tried, which promised to be more satisfactory, because, *inter alia*, it permitted the proper support of a naked wire inside the bulb. The essential features of this seal are shown in Fig. 4. The glass tube was constricted to allow the tinned copper electrode to pass through neatly without play. The upper part of the glass was heated nearly to redness and molten lead poured into the tube; the lead chilled so quickly at the constriction that it solidified there and prevented passage of lead into the bulb. The preliminary tests were carried out on single joints, which were sealed to the pump and evacuated. It is interesting to observe that where the glass had been hot, lead which had overflowed on the outside of the tube adhered strongly to the glass and at the colder portions of the tube the lead peeled off quite easily.

After some practice, a satisfactory seal was obtainable and a T-shaped bulb was constructed using this type of joint for the electrode seals. In this bulb the tungsten wire was stretched between the two electrodes and a supporting capillary tube was unnecessary.

One end of each copper electrode was hammered flat and folded into a small trough; then the end of the wire was laid along the trough and secured by hammering the sides together. Good electrical contact and a secure hold for the wire were thus obtained. The electrode and wire were passed through one side tube of the bulb; the upper electrode was then sealed in with molten lead, and finally the bulb was reversed and the second electrode similarly sealed in. This bulb was connected to the pump and evacuated; the following figures show the efficiency of the seals.

28/12/23	4 p.m.	Pressure = 0·0003 mm. of mercury.
8/1/24	10 a.m.	Pressure = 0·0080 „ „ „

Thus these seals, while useful for many purposes, did not appear tight enough for the present experiments.

At this stage it was decided to conduct several explosions, using the highest vacuum attainable, with a number of bulbs, having molybdenum–glass seals, which had been prepared. The electrode seals were coated externally with sealing wax in such a manner as to give an even, well melted coating of wax: such coatings had been found to enable the bulbs to hold very high vacua, and were really excellent except that they precluded strong heating of the bulb during evacuation. A bulb was evacuated to the limit of the pump,

being heated meanwhile to about 100° by means of a soft, luminous gas flame. The evacuated bulb was allowed to stand over-night on the pump, and the state of the vacuum noted. In each case a single stroke of the pump removed a minute bubble, so small that it could not be driven down the capillary fall-tube of the pump. The bulb was again heated and another stroke of the pump showed that no gas had been released from the glass: it was then sealed off at the vertical capillary.

The Explosions.

Messrs. A. Reyrolle & Co. Ltd., electrical engineers, of Hebburn-upon-Tyne, very courteously placed their high-tension testing plant at our disposal and we desire to record here our thanks to Mr. H. W. Clothier and Mr. Harle for their interest and active co-operation in carrying out the experiments at their works.

FIG. 5.

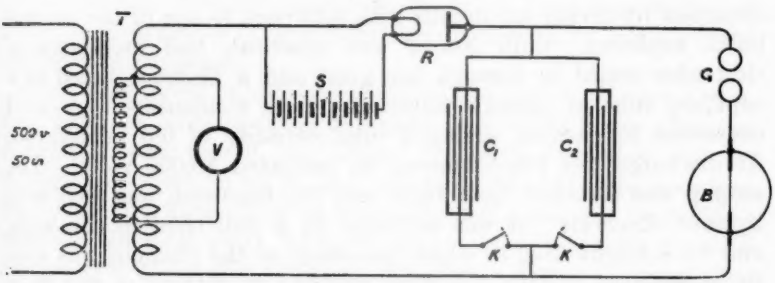


Fig. 5 is a diagram of the circuit used. The two condensers, C_1 C_2, each consisted of 100 glass plates, 24 inches square, having on each face tinfoil coatings 18 inches by 17 inches: the plates were carried on porcelain insulators in a wooden frame: heavy brass leads connected alternate coatings with two copper busbars on opposite sides of the condenser. The condensers were not oil-immersed. Each had a capacity of 0·3 microfarad, the normal working pressure was 30,000 volts, and the highest permissible pressure was 45,000 volts. The connexions permitted the use of either condenser singly or of both in parallel.

Current at 500 volts and 50 cycles A.C. from the supply mains fed to the transformer, T, was stepped up to any desired voltage (up to a maximum of 100,000 volts) and the output was rectified by a two-electrode thermionic valve, R, the filament current for which was supplied by the accumulator, S. The knife switches, K, being closed, this rectified output charged the condensers. When the potential difference across the condensers reached a certain

value dependent on the width of the adjustable air-gap, G, between two large polished brass spheres, the condensers discharged across the gap and through the bulb B. The whole of this apparatus was contained in a large cage of expanded steel, well earthed, and the necessary switches were actuated from the outside of the cage.

A kilovoltmeter, V, across a tertiary winding of the transformer gave an approximate indication of the discharge potential. Throughout the experiments the spark-gap was kept constant and at the conclusion of the tests a precise measurement showed that the potential difference required for discharge across the gap was 29,000 volts.

In one case, contact between the leads and the electrodes of the bulb was made through mercury contained in rubber tubing slipped over the latter. This bulb fractured on discharge, probably because this method of securing contact was defective, and the other bulbs were connected up in turn by twisting the leads tightly round the external parts of the electrodes.

The phenomena associated with the explosions may best be described by giving the details with reference to one of the several bulbs exploded. Bulb No. 4 was spherical, had molybdenum electrodes sealed in through the glass and a filament fitted in a capillary tube as already described. Both condensers were used connected in parallel, giving a total capacity of 0·6 microfarad. At discharge, the kilovoltmeter, K, indicated 30,000 volts. The air-gap was screened from sight and the explosion was well seen by four observers: it was attended by a dull thud in the bulb, and by a bright flash in which the whole of the filament was seen to be involved. Both the noise and the brightness of the flash were much less than we had anticipated.

On examining the bulb, it was found that the filament had completely disappeared: the capillary, now loose in the bulb, was intact, showed a mere trace of a metallic mirror at one end, and was slightly bent at both ends, having evidently been softened there by heat.

It will be remarked that these effects differ substantially from those described by Wendt and Irion: we nevertheless regarded this explosion as complete and satisfactory.

Within a few hours after explosion, the contents of the bulbs were investigated. An induction coil discharge was passed between the supplementary electrode, F, and one of the main electrodes, and the light emitted in the capillary tube, C, was examined visually with a Hilger constant deviation spectrometer. In each of the bulbs there was a small amount of gas which permitted a discharge to pass and gave a faint banded spectrum on which were superposed a few bright lines, the wave-lengths of which were read directly

on the spectrometer drum. The lines observed were the green lines of mercury and the red and blue hydrogen lines; none of the bulbs at any time gave any yellow line whatever, although the spectrometer showed the two sodium lines bright and well defined in the light from an ordinary Bunsen flame.

We conclude, therefore, that our experiments afford no evidence that tungsten can be made to yield helium when exploded by an electrical discharge. At the same time, it is clear that extreme difficulties attend any attempt at a crucial experiment on these lines, and we attach much more importance to experiments now in progress on the electrical explosion of tungsten wires in relatively dense and non-conducting atmospheres of absorbable gas.

Our conclusion is supported by the results, published since our tests were completed, of a similar series of experiments conducted in Dr. Anderson's laboratory (Sinclair Smith, *Proc. Nat. Acad. Science*, 1924, **10**, 4). This investigator encountered difficulties in the construction of gas-tight containers, and in attaining satisfactory vacua, precisely similar to those we have described, but he finds no evidence of any formation of helium by the electrical explosion of tungsten.

A still more recent publication (Harkins and Allison, *J. Amer. Chem. Soc.*, 1924, **46**, 814) describes experiments in which heavy electrical discharges were passed (a) *between* fine wire electrodes, and (b) through fine metallic wires, and the gases (if any) were examined for helium by absorption in heated metallic calcium by Soddy's method. In most cases, the gas was completely absorbed and in no case was there any evidence of helium. Hence it seems clear that the statements made by Wendt and Irion must be attributed to erroneous observations and have no foundation in fact.

Our thanks are due to the Chemical Society for a grant which has defrayed the major part of the expenses incurred in this investigation and to the Department of Scientific and Industrial Research for a grant enabling one of us (G. E. S.) to take part therein.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE UPON TYNE. [*Received, November 24th*, 1924.]

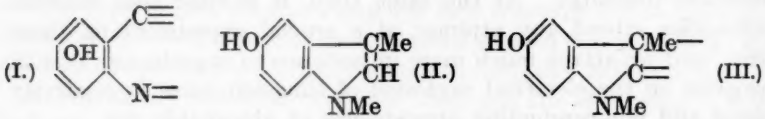
XLII.—*Physostigmine (Eserine). Part III.*

By EDGAR STEDMAN and GEORGE BARGER.

CERTAIN details of the structure of physostigmine have been elucidated (J., 1923, **123**, 758; 1924, **125**, 1373), but the evidence which was available was insufficient to permit the construction of

a formula which satisfactorily represented the known facts concerning the chemistry of this alkaloid. Further experimental evidence is now advanced, and this, combined with previously published work, appears to leave no doubt as to the structure of eserethole and hence of physostigmine, which are respectively the ethyl ether and methylcarbamido-derivative of eseroline.

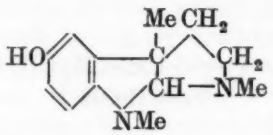
The presence in eseroline of the grouping I has been recognised

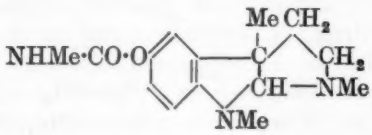


since the work of Straus (*Annalen*, **1913**, **401**, 350; 1914, **406**, 332), who obtained a phenolic indole compound (physostigmol) by degradation of eseroline methiodide. It was shown by one of us (E. S.; *loc. cit.*, 1373) that physostigmol is 5-hydroxy-1 : 3-dimethylindole (II), and further that its ethyl ether may be obtained in a yield of 66% by distillation of eserethole methiodide. This established the position of the hydroxyl group in eseroline and also confirmed Straus's supposition that physostigmol contains a methyl group attached to position 3 of the indole ring. The formation of an indole compound by the somewhat violent decomposition of an alkaloid does not, in general, permit the conclusion to be drawn that a preformed indole skeleton exists in the latter. Nevertheless, it appears justifiable, in view of the comparative completeness with which eserethole methiodide is degraded into physostigmol ethyl ether, to assume, even without further evidence, the presence of the grouping III in eseroline. Additional evidence pointing to the presence of an indoline grouping in the molecule is not, however, wanting. Thus, the feebly basic properties of one of the nitrogen atoms in physostigmine (Straus, *loc. cit.*) and the properties of etheserolene, obtained by Max and Michel Polonovski (*Bull. Soc. chim.*, 1918, [iv], **23**, 335; 1923, [iv], **33**, 969) by the exhaustive methylation of eserethole, point in this direction.

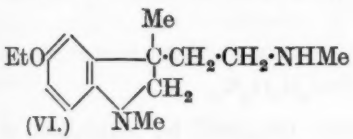
The presence of the grouping III may thus be regarded as established, and the problem resolves itself into determining the manner in which the remainder of the molecule (C_3H_8N) is linked to this grouping. The nitrogen atom, the position of which has still to be determined, is the one with the stronger basic properties. Straus has shown that one methyl group is attached to this nitrogen atom, whilst Salway (J., 1912, **101**, 978) had previously demonstrated its tertiary character. Formula IV, which was suggested to us by Professor R. Robinson, F.R.S., conforms to these conditions, and evidence will be adduced in the following discussion

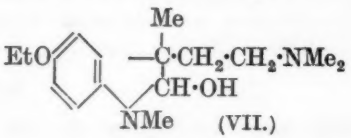
to show that this actually represents the structure of eseroline. The constitution of physostigmine itself will accordingly be represented by formula V.

(IV.) 

 (V.)

The considerations which have led to the adoption of formula IV for eseroline are largely based on the behaviour of eserethole towards reducing agents and on the properties of eseretholemethine. Polonovski (*Bull. Soc. chim.*, 1918, [iv], **23**, 357) has shown that eserethole, on reduction with zinc and hydrochloric acid, takes up two atoms of hydrogen, a result which has now been confirmed using a catalytic method of reduction. That this reduction is not due to the presence of a double bond follows from the fact, first pointed out by Max and Michel Polonovski (*Compt. rend.*, 1924, **178**, 2078), that, whereas eserethole is a tertiary base, dihydroeserethole is a secondary base. Reduction evidently opens a ring between the more strongly basic nitrogen atom and one of its adjacent carbon atoms. On the basis of IV, dihydroeserethole may thus be represented by VI, the point at which the ring is ruptured being deter-

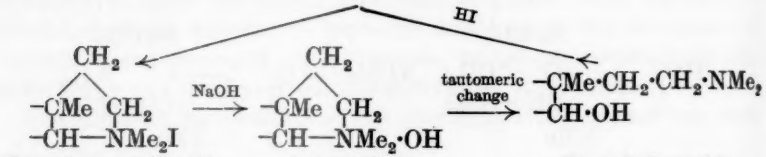

(VI.)


(VII.)

mined from Polonovski's observation that the substance obtained by reduction of etheserolene is identical with the product of the exhaustive methylation of dihydroeserethole.

Eseretholemethine was obtained by Max and Michel Polonovski (*loc. cit.*) by treating eserethole methiodide with sodium hydroxide. Its pseudo-basic character was not recognised until, in Part I of this series, attention was directed to the fact that it is reconverted into eserethole methiodide on treatment with hydriodic acid, and that its behaviour in this respect was analogous to that of certain indoline compounds prepared by Brunner. As a result of this observation, Polonovski revised the molecular formula of eseretholemethine and demonstrated that it was produced from methyleseretholinium hydroxide by a tautomeric change and not by loss of water. Experimental results, which are enumerated in the succeeding paragraph, have now been obtained which demonstrate that eseretholemethine is, in fact, a substituted indoline with a

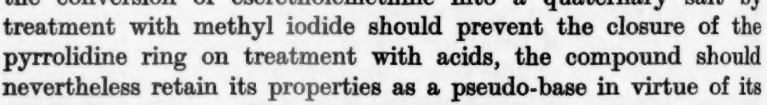
hydroxyl group in the α-position (VII); its formation may accordingly be represented by the following scheme:



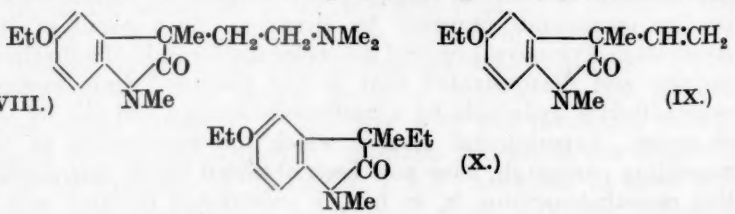
Eserethole methiodide — Intermediate quaternary hydroxide — Eseretholemethine

The position assigned to the basic nitrogen atom in V thus corresponds with this behaviour.

Assuming the correctness of this scheme, it is evident that while the conversion of eseretholemethine into a quaternary salt by treatment with methyl iodide should prevent the closure of the pyrrolidine ring on treatment with acids, the compound should nevertheless retain its properties as a pseudo-base in virtue of its indolinol structure. This consequence has been verified. Treatment of eseretholemethine methiodide with picric acid results in the elimination of the hydroxyl group with the formation of a diquaternary picrate:

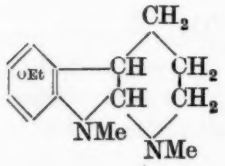


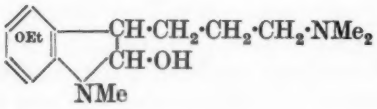
Still more conclusive are the results obtained by oxidation of eseretholemethine. Brunner (*Monatsh.*, 1896, **17**, 253) has shown that 1 : 3 : 3-trimethyl-2-indolinol is oxidised by ammoniacal silver nitrate in alcoholic solution to 1 : 3 : 3-trimethyl-2-indolinone. By subjecting eseretholemethine to the same treatment, a compound the composition of which corresponds with VIII has been obtained. The same substance has also been prepared by oxidising eseretholemethine with potassium ferricyanide, a method which Decker (*J. pr. Chem.*, 1893, **47**, 28) has employed for the oxidation of pseudo-bases. When this compound is degraded by the method of



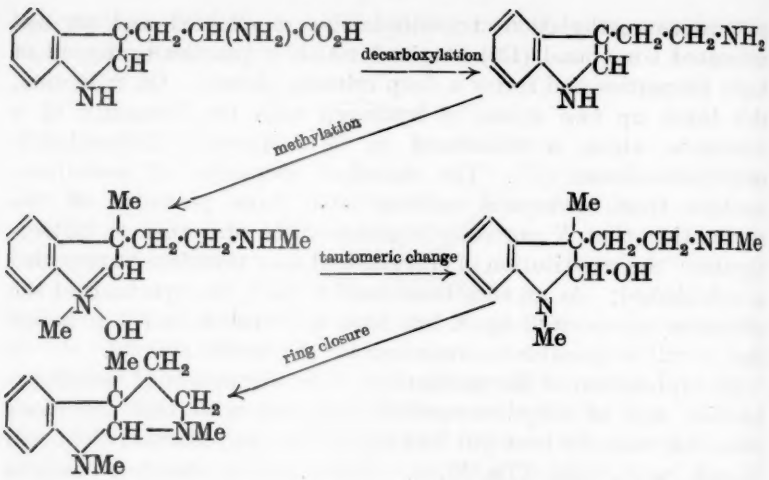
exhaustive methylation, trimethylamine is evolved and an unsaturated compound (IX) obtained which is practically devoid of basic properties and forms a deep crimson picrate. On reduction, this takes up two atoms of hydrogen with the formation of a substance which is considered to be 5-ethoxy-1 : 3-dimethyl-3-ethyl-2-indolinone (X). The chemical properties of eseretholemethine thus correspond entirely with those predicted on the assumption that V correctly represents the structure of physostigmine; the constitution of this alkaloid may therefore be regarded as established. As an additional confirmation, the synthesis of the substance represented by X has been undertaken and it is hoped that it will be possible to communicate the results shortly.

An explanation of the mechanism of the formation of eseretholemethine and of dihydroeserethole identical with that advanced above has recently been put forward by Max and Michel Polonovski (*Compt. rend.*, 1924, **178**, 2078). These authors therefore consider that the structures of eserethole and eseretholemethine are represented by XI and XII, respectively; the former differs from that proposed by Straus (*loc. cit.*) for eseroline only in the position of the nitrogen atom contained in the piperidine ring. Although the reactions described in this communication could be formulated with equal facility upon the basis of these structures, it is evident that they do not explain the formation of physostigmol; the ease with which this substance is formed demands the presence of a preformed methyl group in the β-position of the pyrroline ring.

(XI.) 

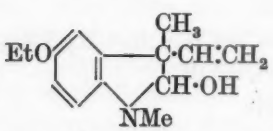

(XII.)

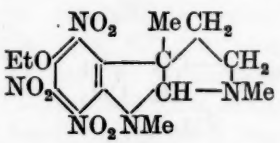
Consideration of the possible mechanism of the phytochemical synthesis of the ring system present in physostigmine speaks no less convincingly in favour of formula V. Perkin and Robinson (J., 1919, **115**, 944) have shown how harmine may be elaborated in the plant from tryptophan. If the assumption is made that the methylation of an indole nucleus may proceed in the plant in the manner in which it is known to take place in the laboratory, a relation between physostigmine and this amino-acid at once becomes evident. By decarboxylation and methylation, followed by a ring closure, the ring system of physostigmine would be readily formed :



The possible mechanism of the phytochemical synthesis of the ring system present in XI cannot be similarly represented in a simple manner from known naturally-occurring substances.

During the course of this investigation a small quantity of etheserolene was prepared. Contrary to Polonovski's statement, it readily formed a yellow, crystalline picrate. If etheserolene is formed by a straightforward degradation of eseretholemethine in a manner similar to that of the indolinone compound now described, one would feel inclined to attribute to it the structure represented by XIII. On this basis, however, it should possess the properties

(XIII.) 



(XIV.)

of a pseudo-base. But analysis of the picrate shows that this is not the case. It therefore appears that some isomeric change has taken place during its formation. This would correspond with the results of Polonovski, who has recently stated (*Compt. rend.*, 1924, **179**, 178) that etheserolene, on reduction, absorbs only two atoms of hydrogen and at the same time loses an atom of oxygen. Whether his view that this oxygen atom is not present as a hydroxyl group, but forms part of a ring, is correct, cannot be stated with certainty at present.

Trinitroeserethole (XIV) and an oxidation product of eserethole which have been prepared during the course of this investigation and the results of a reinvestigation of the degradation of one of the

esoline compounds described in Part I of this series are described in the experimental portion.

Experimental.

Dihydroeserethole (VI).—Attempts to reduce eserethole catalytically with a palladium sol in either neutral or acid solution, with or without the addition of gum arabic as protective colloid, were unsuccessful, owing to flocculation of the sol. With platinum black prepared by Willstätter's method (*Ber.*, 1921, **54**, 113), reduction took place readily. Platinum black (0·1 g.) was washed into a hydrogenation apparatus similar to that described by Hess (*Ber.*, 1913, **46**, 3113), air was completely removed, a solution of 1 g. of eserethole in glacial acetic acid introduced, and the mixture shaken; 52 c.c. of hydrogen were absorbed during the first hour, and 92 c.c. in all (calculated for two atoms : 91 c.c.). The solution was filtered, made alkaline with sodium hydroxide, and the oil thus thrown down extracted with ether. From the extract dried over potassium carbonate a yellow oil was obtained which became almost colourless when distilled under the vacuum of a rotatory oil pump (bath at about 200°). When treated with alcoholic oxalic acid, it formed an oxalate (sheaves of fine needles, m. p. 204°, from aqueous alcohol), identical with that obtained from dihydroeserethole prepared by Polonovski's method (*loc. cit.*).

Dihydroeserethole (1 g.) was heated in a sealed tube with excess of methyl iodide for 1 hour at 100°, the excess of methyl iodide evaporated, and an alcoholic solution of the product treated with alcoholic picric acid. The yellow picrate precipitated on addition of water crystallised from aqueous alcohol in prisms, m. p. 204° (Found : C = 47·0; H = 4·7. $C_{29}H_{34}O_{15}N_8$ requires C = 47·3; H = 4·6%). The substance was thus a *dipicrate*, and two methyl groups had been introduced into the molecule during methylation, indicating that, in contrast to eserethole, dihydroeserethole is a secondary base.

Behaviour of Eseretholemethine Methiodide as a ψ-Base.—The orange oil which separated on mixing the salt (0·2 g.) and picric acid in alcoholic solution changed, on warming, into a crystalline solid (0·27 g.), which was obtained from aqueous alcohol in yellow prisms, m. p. 170° (Found : C = 47·7; H = 4·7. $C_{29}H_{32}O_{15}N_8$ requires C = 47·5; H = 4·4%). In the formation of this di-quaternary picrate, water has been eliminated from the molecule, thus indicating the pseudo-basic function of the oxygen atom.

Dehydroeseretholemethine (VIII).—The methine (1 g.) was refluxed for 10 hours with an ammoniacal solution of 3 g. of silver nitrate in methyl alcohol. After filtration, evaporation, and dissolution

of the residue in water, ether extracted an insignificant amount of an oil, which formed a crystalline picrate, but was not investigated further. The hot aqueous solution, made faintly alkaline with ammonia, was treated with hydrogen sulphide to remove excess of silver, filtered, boiled to expel ammonia and hydrogen sulphide, and treated with alcoholic picric acid. The viscous precipitate first formed became crystalline on warming and, by fractional crystallisation from aqueous alcohol, gave two picrates, the more soluble one forming needles, m. p. 211° (Found: C = 47·0; H = 4·5. $C_{16}H_{26}ON_2,2C_6H_3O_7N_3$ requires C = 46·7; H = 4·4%), and the less soluble fraction consisting of plates contaminated with some needles. The latter crystallised from acetone in plates, m. p. 199° (Found: C = 52·8; H = 5·4. $C_{16}H_{24}O_2N_2,C_6H_3O_7N_3$ requires C = 52·3; H = 5·4%).

A different result was obtained by the following procedure: An alcoholic solution of eseretholemethine (5 g.) was added to 15 g. of silver nitrate in alcohol made strongly alkaline with ammonia (*d* 0·88), the total volume being brought to about 100 c.c. A silver mirror formed on the sides of the flask almost immediately. The mixture was heated on the water-bath for 5 hours, filtered, and excess of silver removed by addition of hydrochloric acid; from the filtrate, made alkaline with sodium hydroxide, ether extracted 4·45 g. of an oil which, treated with alcoholic picric acid, yielded 5·35 g. of the picrate, m. p. 199°, described above. No trace of the picrate of higher melting point was obtained in this experiment. It seems evident that this substance was formed by reduction of an indolinone to an indoline compound, the reducing agent being the hydrogen sulphide used to remove excess of silver.

Oxidation was also effected by means of potassium ferricyanide. A solution of eseretholemethine (3 g.) in a small quantity of alcohol was boiled with a strongly alkaline solution of 7·2 g. of potassium ferricyanide in 100 c.c. of water for about 5 minutes and after cooling extracted with ether. From this extract, 4 g. of the methiodide which had previously been prepared in the manner described below were obtained.

The picrate (4·19 g.), m. p. 199°, was treated with sodium hydroxide, and the oily base which separated extracted with ether. The extract was dried over sodium sulphate, filtered, concentrated, and methyl iodide added. A crystalline methiodide slowly formed (3·3 g.). This separated from acetone in transparent prisms, but the method was wasteful owing to its large solubility in this solvent. It was therefore crystallised by addition of dry ether to the acetone solution. With dry solvents, the *methiodide* was obtained as a colourless substance, m. p. about 131°; the fact that the melting

point was not absolutely sharp was no doubt due to the water of crystallisation which it contained (Found: for air-dried material, $H_2O = 3{\cdot}7$; for material dried at 110°, I = 30·0. $C_{17}H_{27}O_2N_2I,H_2O$ requires $H_2O = 4{\cdot}1$; $C_{17}H_{27}O_2N_2I$ requires I = 30·1%). When, however, the solvents were not perfectly dry, the transitory formation of a blue iodine adsorption compound was consistently observed; its disappearance no doubt coincided with the transformation of an at first amorphous precipitate into crystalline form.

Degradation of Dehydroeseretholemethine Methiodide by Hofmann's Method to Compound IX.—An aqueous solution of 1·9 g. of the methiodide was shaken with a suspension of silver oxide prepared from 2 g. of silver nitrate. After filtration and removal of the water by evaporation under diminished pressure, the residual oil was distilled at 12 mm. After evident decomposition, with the evolution of a gas, a slightly brown oil distilled when the temperature of the bath was between 200° and 210°. The distillate would not crystallise. It was therefore treated with an alcoholic solution of picric acid, when a small quantity of a crystalline picrate, m. p. 199°, identical with that described above, was obtained. The residue from the mother-liquors was treated with sodium hydroxide and extracted with ether, and the extract washed with water until the sodium picrate was completely removed. After drying over sodium sulphate, the ether was evaporated, when a colourless oil which crystallised spontaneously was obtained. Recrystallised from aqueous alcohol, it formed colourless prisms, m. p. 62° (Found: C = 72·3; H = 7·3. $C_{14}H_{17}O_2N$ requires C = 72·7; H = 7·4%). This substance was practically devoid of basic properties; it was insoluble in dilute hydrochloric acid, but formed a picrate which at first separated from alcohol in a yellow form and quickly changed into a deep crimson one; m. p. 103°.

Reduction of Compound IX to Compound X.—Hydrogenation was effected in the apparatus mentioned above, using a solution of colloidal palladium as catalyst and gum arabic as protective colloid; 0·16 g. of substance was used. Hydrogen was readily absorbed, but as a result of a mishap the amount could not be measured. After filtration from the palladium and evaporation of the alcohol (aqueous alcohol was used as solvent), the solution, after addition of a small quantity of sodium hydroxide to ensure alkalinity, was extracted with ether. After drying and evaporation, this yielded a crystalline product which, when crystallised from aqueous alcohol, formed cubes, m. p. 68° (Found: C = 71·8 H = 8·2. $C_{14}H_{19}O_2N$ requires C = 72·1; H = 8·2%). It is evident from the analysis that two atoms of hydrogen were absorbed and

that the oxygen atom present as a carbonyl group was retained in the molecule.

Trinitroeserethole.—Among the diverse experiments which have been carried out with a view to effect the oxidation of eserethole, the action of nitric acid on this substance has been studied. Cold dilute nitric acid has little, if any, action, but the concentrated acid (*d* 1·4) reacts vigorously. Eserethole (1 g.) was added drop by drop to 3 c.c. of concentrated nitric acid, cooled in a freezing mixture and vigorously stirred. The product was warmed on the water-bath for ½ hour, cooled, diluted with water, and the yellow crystalline precipitate (0·3 g.) recrystallised from aqueous alcohol, *trinitroeserethole* separating in orange, rectangular plates, m. p. 152° (Found: C = 47·1; H = 5·0; N = 18·7. $C_{15}H_{19}O_7N_5$ requires C = 47·2; H = 5·0; N = 18·4%). It is insoluble in alkalis and dilute acids, but dissolves in concentrated acids.

Oxidation of Eserethole with Potassium Permanganate in Acetone Solution.—A solution of eserethole (1 g.) in 100 c.c. of acetone was maintained at about −10° while finely powdered potassium permanganate (representing 6 O) was added during 2 days. The solution was then warmed with methyl alcohol to remove excess of permanganate, filtered, and the solvent evaporated. The red syrup thus obtained would not crystallise even after distillation in a high vacuum, but on treatment with alcoholic picric acid it readily yielded a *picrate* (0·9 g.) which crystallised from alcohol in rhomb-shaped prisms, m. p. 166° (Found: C = 51·8; H = 4·9. $C_{15}H_{20}O_2N_2,C_6H_3O_7N_3$ requires C = 51·5; H = 4·7%). The base was recovered from this picrate by dissolving the latter in glacial acetic acid, pouring into water, and extracting the picric acid with ether, making alkaline with sodium hydroxide and again extracting with ether. The oily base obtained on evaporation of the ether was warmed with methyl iodide and the product dissolved in hot methyl alcohol. On cooling, the *methiodide* crystallised in needles, m. p. 198—199° (Found: C = 48·1; H = 5·8; I = 31·6. $C_{15}H_{20}O_2N_2,CH_3I$ requires C = 47·8; H = 5·8; I = 31·6%). This methiodide resembles eserethole methiodide in its behaviour towards alkalis. It is stable towards sodium carbonate, but when treated with sodium hydroxide yields an ether-soluble base. The latter could not, however, be crystallised, neither could its methiodide be obtained in a crystalline condition.

Etheserolene picrate was prepared incidentally during an experiment designed to test whether the presence of ethyl alcohol or sodium ethoxide was an essential condition for the formation of the esoline compounds described in Part I of this series. Starting from eserethole methiodide, the experimental conditions were

exactly similar to those described in that paper for the preparation of esoline ethyl ether dimethiodide, except that a solution of sodium in *n*-propyl alcohol was used in place of one in ethyl alcohol. No solid separated, however, from the solution. The propyl alcohol was therefore evaporated, the oily residue dissolved in water, made strongly alkaline with solid sodium hydroxide, and the solution refluxed for several hours, tetramethylammonium iodide and an oil volatile in steam separating. The latter, isolated from the mother-liquors by extraction with ether, crystallised in a few hours. The solid, m. p. about 45° (etheserolene, according to Polonovski, melts at 48°), was dissolved in alcohol and treated with alcoholic picric acid, when a yellow picrate separated which crystallised from alcohol in stout prisms, m. p. 98° (Found : C = 52·1; H = 4·9. Calc. for $C_{14}H_{19}O_2N$, $C_6H_3O_7N_3$, C = 52·0; H = 4·8%). From the melting point of the original substance and the analysis of the picrate, it seems evident that this was etheserolene picrate. It is also evident that the oxygen atom has no pseudo-basic function in this compound.

Degradation of Esoline Ethyl Ether Dimethiodide.—The preliminary results of the degradation of this substance by Hofmann's method reported in Part I of this series have been confirmed. Since identical results have been obtained by distillation of the product of the action of silver oxide on the iodide and by treating it with potassium hydroxide, only the latter method need be described. The oil obtained by treating 4 g. of the iodide with silver oxide was refluxed for ½ hour with 10 c.c. of 50% potassium hydroxide. The solution was then steam-distilled until the oil had been completely carried over. The distillate was extracted with ether, upon evaporation of which an oily residue was obtained. This was dissolved in alcohol and the solution treated with picric acid. A viscous picrate separated which slowly solidified on warming. After filtration, this was suspended in a relatively large volume of alcohol, boiled, and filtered. On cooling the filtrate, a *picrate* separated in short, stout prisms, m. p. 156°, unchanged on recrystallisation from aqueous alcohol (Found : C = 46·7; H = 4·7. $C_{16}H_{28}ON_2,2C_6H_3O_7N_3$ requires C = 46·5; H = 4·7. $C_{16}H_{26}ON_2,2C_6H_3O_7N_3$ requires C = 46·7; H = 4·4%). The less soluble *picrate*, which was separated in the manner described above, crystallised from aqueous alcohol in rhomb-shaped prisms, m. p. 199° (Found : C = 46·9; H = 4·7. $C_{18}H_{30}O_2N_2,2C_6H_3O_7N_3$ requires C = 47·1; H = 4·7. $C_{18}H_{28}O_2N_2,2C_6H_3O_7N_3$ requires C = 47·2; H = 4·5%). Both picrates were converted into methiodides by the following treatment. The picrate was dissolved in glacial acetic acid, poured into water, extracted with ether to remove

picric acid, made alkaline with ammonia, and the base extracted with ether. Addition of methyl iodide to the ethereal solution (dried over sodium sulphate) caused the methiodide to separate. The picrate melting at 156° thus yielded a methiodide which crystallised in plates, melted at 169—170°, and was identical with a methiodide which had been obtained directly from the crude product of the distillation of the quaternary hydroxide without purification through the picrate (Found: C = 50·2; H = 7·4. $C_{17}H_{31}ON_2I$ requires C = 50·2; H = 7·6. $C_{17}H_{29}ON_2I$ requires C = 50·5; H = 7·2%). The picrate melting at 199° yielded a methiodide, m. p. 141°; when this was heated at 100° in a sealed tube for ½ hour with excess of methyl iodide, a second methiodide, m. p. 188°, was obtained, but no esoline ethyl ether dimethiodide was formed. Apparently this base was not, as was originally believed, the ethyl ether of the hypothetical esoline base.

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XLIII.—*The Action of Light on the Ferrous Ferric Iodine Iodide Equilibrium.*

By ERIC KEIGHTLEY RIDEAL and EDWARD GARDNER WILLIAMS.

THE exceptions to Einstein's laws of photochemical equivalence may be divided into two classes according as the number of quanta absorbed is (1) greater than the number of molecules decomposed, the excess quanta being emitted as fluorescence or dissipated in heating the reacting system, or (2) less than the number of molecules decomposed. In class (2), chain reactions occur of the atom type as is exemplified in the reactions $Cl + H_2 = HCl + H$ and $H + Cl_2 = HCl + Cl$ (Nernst, *Z. Elektrochem.*, 1918, **24**, 335), or the product of the reaction with the original energy of excitation together with the energy liberated by the reaction may excite other molecules on impact (Christiansen and Kramers, *Z. physikal. Chem.*, 1924, **104**, 452) as, *e.g.*, in the chorination of toluene at low temperatures without a chlorine carrier (Book and Eggert, *Z. Elektrochem.*, 1923, **340**, 521). It is to be anticipated that if a photosensitive system could be formed in which chain reactions of either of these ssort could be eliminated the Einstein law of photochemical equi-

valence would be obeyed. Conditions for such evidently obtain in systems in which the energy may be rapidly dissipated, no atom chains being formed, and in which the energy of excitation is relatively small.

It has long been known that the interaction between ferric salts and iodides to produce ferrous ions and free iodine is reversible and that the reaction expressed by the equation

$$2Fe^{\cdot\cdot\cdot} + 2I' \underset{\text{light}}{\overset{\text{dark}}{\rightleftharpoons}} 2Fe^{\cdot\cdot} + I_2$$

is photosensitive. Sasaki (*Mem. Coll. Sci. Kyoto*, 1922, **5**, 5) has shown more recently that under conditions of uniform illumination with light from an electric lamp a photochemical equilibrium different from the dark equilibrium is attained.

It was considered that this reaction might reasonably be expected to obey the Einstein law of photoequivalence. An investigation of the photodynamics of the system revealed the fact that this law was rigidly fulfilled, the mechanism of the reaction being expressible in the form

$$\begin{matrix} I' \\ I' \end{matrix}\!\!\diagdown\!\!Fe^{\cdot\cdot} + Fe^{\cdot\cdot}\!\!\diagup\!\!\begin{matrix} I' \\ I' \end{matrix} + h\nu = \begin{matrix} I' \\ I' \end{matrix}\!\!\diagup\!\!Fe^{\cdot\cdot\cdot} + Fe^{\cdot\cdot\cdot}\!\!\diagdown\!\!\begin{matrix} I' \\ I' \end{matrix} + I' :$$

$$I - I' - I$$

and that the minimum value of a photochemically active quantum corresponded to a wave-length $\lambda = 5790$ Å. or a potential of 2·14 volts.

Further investigation indicated that the photosensitive constituent was the iodine; both the iron salts and the iodine ion being inactive over the region of spectrum employed. The value of the quantum determined in this way, $\lambda = 5790$ Å., $E = 49{,}200$ cals. per gm.-mol., or $V = 2{\cdot}14$ volts, agrees very closely with the resonance potential of the iodine molecule, $2{\cdot}34 \pm 0{\cdot}2$ volts, as determined by Foote and Mohler ("The Origin of Spectra," p. 78), thus supporting the evidence obtained from this investigation that the photochemical action results from the optical excitation of the iodine, and that the level of energy corresponding to the resonance potential of the iodine molecule is also a chemically active state of excitation.

Experimental.

(a) *Isolation of the Photochemically Active Light of Minimum Quantum Value.*

Equal volumes of two solutions of the compositions, (A) Ferric ammonium alum 0·02 molar, ammonium sulphate 0·02 molar,

made up to $N/10$ by the addition of sulphuric acid, and (B) potassium iodide 0·09 molar, were mixed. The following reaction occurs:

$$Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O + (NH_4)_2SO_4 + 4{\cdot}5KI + 5H_2SO_4 \rightleftarrows 2FeSO_4 + 2(NH_4)_2SO_4 + K_2SO_4 + I_2 + 2{\cdot}5KI + 5H_2SO_4.$$

The liberation of iodine proceeds rapidly at the start in the dark, and equilibrium is almost attained at the end of 24 hours, but a slow reaction goes on for several weeks.

As source of light, a 1000 c. p. gas-filled lamp (110 volts, 10 amps.) was employed in conjunction with a series of "M" light filters (Wratten type) for isolating comparatively narrow regions of the spectrum. The cuts of these filters as published by the makers were confirmed by means of a direct-vision spectroscope and found to be accurate under the conditions of the experiment. Both the gelatin light filter and the flat-sided, glass-stoppered reaction vessel were maintained at a uniform temperature of 25° in glass-sided troughs by means of a water-circulating system from a controlled thermostat. In order to obtain approximate equality of intensity in the transmitted light, the distance of the lamp from the filter was changed for each combination of filters according to their transmission as published by the makers.

To follow the change in equilibrium, the amount of iodine in solution was estimated by titration of 5 c.c. of solution run into 100 c.c. of water at 0° with approximately $N/200$-sodium thiosulphate solution, using starch as indicator. The usual precautions concerning the quantity of starch and standardisation of the weak thiosulphate solution were taken. The following results were obtained:—

Filter.	Wave-length in Å. of light transmitted.	Exposure in hours.	Titration value for the unilluminated solution in c.c. less that for illuminated.
A + C	6500—7000	2	0
F	6000—7000	2	0·60
B + E	5000—6300	2	0·80
C	4000—5100	2	0·15
G + H	5100—5500	2	0
D + H	4300—4700	2	0
B + C	4870—5040	2	0
White		1	8·75

The region of the spectrum responsible for the photochemical change appears from these data to lie between $\lambda = 5500$ and 6500 Å.

The quartz mercury vapour lamp emits a group of strong yellow lines at about $\lambda = 5790$ Å., which can be isolated conveniently by means of a colour filter prepared by the Kodak Co. Replacing the 1000 c. p. lamp by a quartz mercury vapour lamp, the following data were obtained, the time of exposure being in all cases 2 hours.

Filter.	Light transmitted in A.	Titration value in c.c. $N/200$-thio.
Nil	Complete spectrum	6·6
E	5790, 5769, 5679 (and red lines)	1·05
C	4916—4078, 4047	0
H	5461, 4916, 4359, 4348, 4339	0
Mercury green 2% yellow	5461	0·20

These results confirm those obtained with the 1000 c. p. electric lamp and show that, in addition to the ultra-violet light, the lines 5790, 5769, 5679 are photochemically active (the red lines, although absorbed by the solution, being very faint, contributed but little, if any, energy to the system). The line $\lambda = 5790$ Å. corresponds to an energy of excitation of 49,200 calories or a potential of $V = 2{\cdot}14$ volts, a value, as we have seen, almost identical with the resonance potential of the iodine molecule.

(b) *The Photochemically Active Constituent.*

As has already been indicated, it would appear from the above experiments that the iodine was the photochemically active constituent. Since we are dealing with a reversible system, any alteration in the equilibrium constant would entail a relative alteration in the velocity coefficients of the two reactions :

$$(1)\ I_2 + 2Fe^{\cdot\cdot} \longrightarrow 2Fe^{\cdot\cdot\cdot} + 2I' \quad k_1$$
$$(2)\ 2I' + 2Fe^{\cdot\cdot\cdot} \longrightarrow 2Fe^{\cdot\cdot} + I_2 \quad k_2$$

It was accordingly important to find out whether this apparent relative alteration in the velocity coefficients under illumination was produced by the actual alteration in k_1 and that k_2 remained unaltered under illumination.

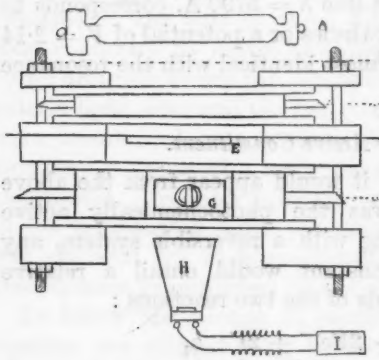
In order to establish this point a modification of the Harcourt and Esson experiment as used by Donnan and Le Rossignol (J., 1903, **83**, 703) to determine the order of reaction between the ferricyanide and iodide of potassium was employed. Fifty c.c. of the iodide solution B to which 2 c.c. of a standard thiosulphate solution and two drops of starch solution had been added were placed in a vessel provided with a stirrer and maintained at 25° in a thermostat. An equal volume of the ferric iron solution A at 25° was added and the time of appearance of the blue colour noted. Immediately on its appearance, a fresh quantity of thiosulphate solution was added and the time of reappearance of the starch iodine blue observed. With the precautions as to strength of solution and use of the delivery pipette given by Donnan and Le Rossignol, the reaction was carried out at 25° in the dark and in the light of the 1000 c. p. electric lamp. The rates of reaction both in the dark and under illumination were found to be identical.

In the above reaction the iodide-ion concentration was maintained constant during the conversion of the ferric into ferrous ion, and the system is insensitive to illumination. Thus the alteration in the equilibrium of the system under illumination is due to an increase in the velocity of the reaction :—

$$I_2 + 2Fe^{\cdot\cdot} \longrightarrow 2Fe^{\cdot\cdot\cdot} + 2I'.$$

If the increase in the velocity coefficient of this reaction under illumination were due to a photochemical increase in the chemical activity or thermodynamic concentration of the iodine molecules, we should anticipate that a simple concentration cell of the type

FIG. 1.



$$\begin{array}{ccc} \text{Pt} & & \text{Pt} \\ | & I_2 \text{ in KI} \;|\; \text{KI} \;|\; I_2 \text{ in KI} & | \\ & \text{Dark.} \qquad \text{Illuminated.} & \end{array}$$

should exhibit a definite electromotive force. Such cells constructed with platinum electrodes and various strengths of iodine solutions in potassium iodide showed after removal of all traces of dissolved oxygen no electromotive force on illumination of one half of the cell. It therefore seems probable that the production of excited iodine molecules by the photochemical action is small compared with the rate at which the reaction $2\epsilon + I_2 \rightleftarrows 2I'$ occurs at the electrode.

(c) *The Application of the Einstein Law of Photoequivalence.*

For the determination of the amount of radiation absorbed and the concomitant chemical action produced by the radiation the following apparatus was employed (Fig. 1) :

A. Mercury vapour lamp. B. Screen. C. Cooling trough. D. Blackened metal plate carrying gelatin light filter, E. F. Cooling trough containing glass-stoppered reaction vessel, G. H. Moll thermopile. I. compensating leads and galvanometer.

The Moll thermopile, H, was first calibrated by means of a Leslie cube, precautions being taken to ensure "black body" radiation as nearly ideal as possible in the circumstances by screening the system of Leslie cube and thermopile with non-conducting material faced with reflecting surfaces in which accurate openings were cut. The radiant energy received by the thermopile from the Leslie cube was calculated by the formula of Lummer and Pringsheim, (*Ann. Physik*, 1897, **63**, 395) and found to be $1{\cdot}23 \times 10^5$ ergs per sec.

The readings of the galvanometer connected to the thermopile during the radiation fluctuated slightly between 35·4 and 36·4 cm., yielding a mean value of 35·95 cm.

Hence the energy per cm. deflection is $3{\cdot}423 \times 10^3$ ergs per second. Allowing for the fact that lamp-black surfaces emit and absorb but 90% of the true black-body radiation, the thermopile constant is $2{\cdot}77 \times 10^3$.

The volume of the solution in G covered by the funnel of the thermopile was found both by measurement and by calculation to be 31 c.c.

The mercury vapour lamp was started and allowed to attain a steady state, the current being checked by means of an ammeter connected in the circuit. The thermopile, suitably protected from draughts, was allowed to come into equilibrium with its surroundings, precautions being taken to keep the room temperature as steady as possible. The bottle was first filled with water and a number of readings were taken of the deflection caused on the galvanometer scale when the screen B was raised. The bottle was then filled up to the mark with the dark equilibrium solution, and a number of readings taken as before.

Since, even with the utmost precaution, mercury vapour lamps are apt to vary in intensity of illumination, a number of independent experiments were performed, of which the two appended represent the extremes of variation. The curve of the rate of disappearance of iodine under the same conditions was also obtained, by means of a large number of experiments which agreed fairly closely.

Water.

	Deflection on galvanometer scale in cm.		Total deflection in cm.	
	Initial.	Final.		
(I)	7·3	27·8	20·5	Mean = 20·37
	7·2	27·5	20·3	
	7·0	27·5	20·5	
	7·0	27·2	20·2	
(II)	5·4	27·8	22·4	Mean = 22·53
	5·6	28·2	22·6	
	5·6	28·2	22·6	

Dark equilibrium mixture.

(I)	6·9	15·1	8·2	Mean = 8·1
	7·0	15·0	8·0	
	6·9	14·8	7·9	
	7·0	15·3	8·3	
(II)	5·4	13·7	8·3	Mean = 8·5
	5·6	14·2	8·6	
	5·4	14·0	8·6	

Energy absorbed by solution in (I) = $12{\cdot}3 \times 2{\cdot}77 \times 10^3$ ergs per second.
Energy absorbed by solution in (II) = $14{\cdot}03 \times 2{\cdot}77 \times 10^3$ ergs per second.
Mean = $13{\cdot}2 \times 2{\cdot}77 \times 10^3$ ergs per second.

The rate of disappearance of iodine under the same conditions was next investigated.

At various times, 5·15 c.c. were withdrawn, run into 100 c.c. of cold water, and titrated with approx. $N/100$-thiosulphate, the following data being obtained from which the velocity coefficient $[k = 1/t.\log a/(a - x)]$ has been calculated : $a = 7{\cdot}5 \times 0{\cdot}0012696$ g. of I_2.

T (mins.).	$N/100$-Thio. (c.c.).	t.	x.	k.
0	7·50	15	0·0006345	0·00463
15	7·14	30	0·001142	0·00430
52	6·20	60	0·002030	0·00404
120	5·40	90	0·003173	0·00455
192	4·97			
422	4·91		Mean =	0·00438

The reaction appears to follow the unimolecular law as indicated by the values of k, hence the initial rate of disappearance of iodine may be calculated.

$$dx/dt = kc = 0{\cdot}00438 \times 0{\cdot}000005 \times 7{\cdot}5 \times 6{\cdot}06 \times 10^{23}$$
molecules I_2 per minute for 5·15 c.c.
$$= 0{\cdot}996 \times 10^{16} \text{ molecules } I_2 \text{ per sec. for 31 c.c.}$$

We can now proceed to calculate the number of quanta absorbed per sec. by the solution.

Wave-length = 5790·66 Å. Frequency $\nu = 5{\cdot}176 \times 10^{14}$.
Magnitude of quantum $= h\nu = 6{\cdot}55 \times 10^{-27} \times 5{\cdot}176 \times 10^{14}$
$$= 3{\cdot}39 \times 10^{-12} \text{ erg.}$$

Energy absorbed by solution $= 13{\cdot}2 \times 2{\cdot}77 \times 10^3$ ergs per sec.
Hence number of quanta absorbed by solution
$$= 1{\cdot}078 \times 10^{16} \text{ per sec.}$$

There are thus $0{\cdot}996 \times 10^{16}$ molecules of iodine being decomposed per second by $1{\cdot}078 \times 10^{16}$ quanta. The reaction thus obeys the Einstein law of photochemical equivalence under the conditions of the experiment.

(d) *The Temperature Coefficient of the Reactions.*

The influence of temperature on the dark equilibrium system

$$2Fe^{\cdot\cdot} + I_2 \rightleftarrows 2Fe^{\cdot\cdot\cdot} + 2I'$$

is negligibly small, but the rate at which equilibrium is attained is very dependent on the temperature; this rate was investigated at 25° and 38·25°, and the equilibrium point was reached in each case, though more rapidly in the warmer solutions. By estimation of the amount of iodine liberated after mixing the solutions A and B

at the two temperatures, the temperature coefficient was calculated from the velocity coefficients to be, for a rise in temperature of 10°, $k_{35°}/k_{25°} = 2{\cdot}713$. The influence of temperature on the rate of attainment of the light equilibrium was investigated by a potentiometric method. A photovoltaic cell consisting of bright platinum electrodes inserted in a constricted U-tube containing the dark equilibrium mixture was employed. On illumination of one limb of the U-tube with monochromatic yellow radiation at 25°, the equilibrium concentration in the exposed limb is altered and the rate of alteration can be determined from the electromotive force of the cell. On cutting off the radiation, the return of the photochemical equilibrium mixture to the dark equilibrium can readily be followed from the electromotive force of the cell. As typical of the readings obtained by this method the following values may be cited.

Temperature 25°.				Temperature 35°.			
Time in mins.	Millivolts.	Time in mins.	Millivolts.	Time in mins.	Millivolts.	Time in mins.	Millivolts.
0	0·0	130	10·30	0	0·0	50	8·60
5	0·9	140	10·30	5	1·40	60	9·25
20	3·05	Light off		10	2·80	70	9·65
40	5·90	142	10·20	20	4·85	80	10·00
60	7·95	145	9·70	30	6·40	90	10·17
75	8·95	150	8·85	40	7·65	100	10·17
90	9·65	185	6·45				
113	10·05	190	6·25				
		200	5·90				

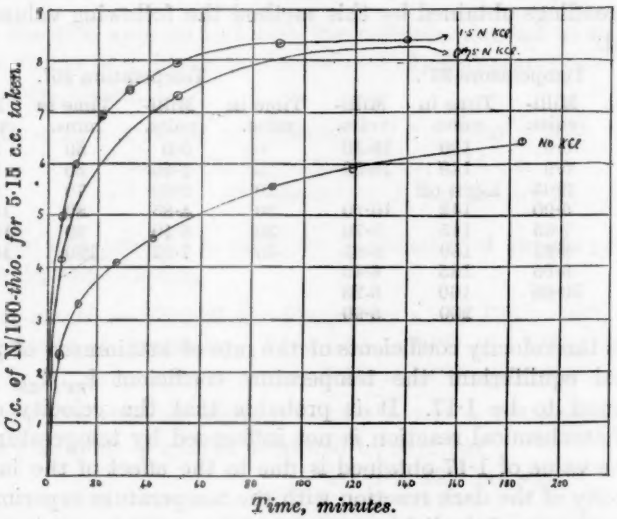
From the velocity coefficients of the rate of attainment of photochemical equilibrium the temperature coefficient $k_{35°}/k_{25°}$ (light) was found to be 1·17. It is probable that the velocity of the true photochemical reaction is not influenced by temperature and that the value of 1·17 obtained is due to the effect of the increase in velocity of the dark reaction with the temperature superimposed on the velocity of the light reaction.

The Influence of Ionic Activities on the Photochemical Equilibrium.

It has already been noted that although the liberation of iodine from the reacting system commences rapidly, yet the reaction comes but slowly to equilibrium. At the end of 24 hours, the average amount of iodine liberated as determined by titration with thiosulphate was found equivalent to 7·80 c.c. of N/100-thiosulphate for 5·15 c.c. of the equilibrium mixture. Although the reaction is apparently completed, nevertheless a slow reaction is still proceeding towards a true equilibrium. This equilibrium was established at the end of 3 months and found equal to 8·37 c.c. of N/100-thiosulphate. Since the equilibrium attained is the result of the attainment of equal velocity for two reactions, $2Fe^{\cdots} + I_2 \rightarrow$

$2Fe^{\cdots} + 2I'$ and $2Fe^{\cdots} + 2I' \longrightarrow 2Fe^{\cdot\cdot} + I_2$, it is clear that if the active masses of equilibrium concentrations of the reactants could be raised in equal proportion the reaction velocities of each reaction would proceed more rapidly and equilibrium would be more rapidly attained. The active masses or thermodynamic concentrations of the active ions, whether simple as indicated above or complex as imagined by Sasaki (*Z. angew. Chem.*, 1924, **137**, 181), can readily be raised by the addition of a neutral salt such as potassium chloride (Brönsted, *Z. physikal. Chem.*, 1922, **103**, 307). In the following curves (Fig. 2) the rate of attainment of equilibrium in the dark for three mixtures to which varying amounts of potassium chloride have been added are given.

FIG. 2.



It is clear from the curves that the augmentation in thermodynamic concentration of the reacting ions by the addition of the potassium chloride has, as anticipated, augmented the rate at which true equilibrium is attained. That the separate reaction velocities are in reality augmented by the addition of potassium chloride was confirmed by repeating the modified Harcourt and Esson experiment as already described in presence of 1·5*N*-potassium chloride and in the ordinary solution without the salt addition. The marked increase in the velocity of the forward reaction on the addition of potassium chloride is evident from the following data:

Time in minutes for appearance of starch-iodide colour.

Thio added (c.c.)	1	2	3	4	5	6	7	8	9
No KCl added	0·5	0·8	1·5	2·8	4·7	8·15	13·7	25·0	
In 1·5*N*-KCl ...	0·4	0·6	1·0	1·6	2·4	3·6	5·6	8·9	16·6

At equilibrium in the dark the rates of the forward photosensitive reactions are given in absence and presence of potassium chloride by the equations $dx/dt = k.f(I_2)f(Fe^{\cdot\cdot})^2 = a$, and $dx'/dt = k.f'(I_2)f'(Fe^{\cdot\cdot})^2 = b$, where f and f' are the activity coefficients in absence and presence of the neutral salt. On illumination of the solutions the respective velocities become

$$dx/dt_{ill.} = k.f(I_2)f(Fe^{\cdot\cdot})^2 + I(I_2) = a + x,$$
$$dx'/dt_{ill.} = k.f'(I_2)f(Fe^{\cdot\cdot})^2 + I(I_2) = b + x,$$

where I is the intensity of the photoactive radiation.

The ratio of the velocities of the two dark and light reactions without and in presence of salt will evidently be,

Without KCl present, $V_{ill.}/V_{dark} = (a + x)/a = 1 + x/a$.
With KCl present, $V_{ill.}/V_{dark} = (b + x)/b = 1 + x/b$.

Thus, the greater the absolute velocity of the forward reaction at equilibrium the smaller will be the apparent effect of the light on the equilibrium. We should thus anticipate that the shift in the equilibrium obtained with the solution containing potassium chloride on exposure to light will be far less than the shift in the equilibrium of the solution in the absence of potassium chloride on exposure to identical radiation, since the addition of salt has, as has been indicated by the previous experiments, raised the value of f' considerably above f, or $b > a$. These expectations were fully realised by determining the rate of change of the dark equilibrium mixture on illumination both by the potentiometric method and by titration. The following data were obtained for a dark equilibrium mixture containing 1·5N-potassium chloride exposed to monochromatic radiation at 25°.

Time (mins.).	Milli-volts.	N/100-Thio. (c.c.).	Time (mins.).	Milli-volts.	N/100-Thio. (c.c.).
0	0	7·86	41	2·40	—
1	0·1	—	52	2·60	—
8	0·8	—	60	2·65	7·30
10	1·05	—	70	2·70	—
25	1·90	—	170	2·70	7·30
30	2·15	7·75			

The final value of 2·70 mv. as compared with a value of 10·3 mv. for the solution in the absence of potassium chloride (see Table, p. 265) and a shift in the equilibrium concentration of iodine equivalent to only 0·56 c.c. of N/100-thiosulphate solution as compared with the value 2·50 c.c. obtained without the potassium chloride, indicated clearly the effect of augmenting the velocity of the two reactions proceeding in either direction at equilibrium by elevation of the thermodynamic concentrations of the reactants.

The value of the equilibrium constant for the reaction

$$K = (Fe^{\cdot\cdot})(I_2)^{\frac{1}{2}}/(Fe^{\cdot\cdot\cdot})(I')$$

has been determined by Maitland (*Z. Elektrochem.*, 1906, **112**, 263) and by Brönsted and Pedersen (*Z. physikal. Chem.*, 1922, **103**, 307). Maitland obtained the value $K = 10^{2\cdot005}$, whilst the data of Brönsted and Pedersen yielded a value of $K_{25^\circ} = 21{\cdot}1$, utilising a value of $L_{25^\circ} = 0{\cdot}00611$ for the equilibrium constant

$$L = (I')(I_2)/(I'_3) = 0{\cdot}0061.$$

The data obtained in the above experiments permit us to calculate the value of K.

The original concentration of ferric ions = 0·02 gm.-atom per litre.
" " " of iodide ions = 0·045 gm.-atom per litre.

The titre of the dark equilibrium solution is 8·37 c.c. of $N/100$-thiosulphate for 5·15 c.c. Hence at equilibrium we obtain :

$$(Fe^{\cdot\cdot\cdot}) = (2{\cdot}0 - 8{\cdot}37/5{\cdot}15)10^{-2} \text{ gm.-atom per litre.}$$
$$(Fe^{\cdot\cdot}) = 8{\cdot}37/5{\cdot}15.10^{-2} \text{ gm.-atom per litre.}$$
$$(I') = 8{\cdot}37/5{\cdot}15.10^{-2} \text{ gm.-atom per litre.}$$

Also, if the original iodide concentration be x and the final $x - a$, we obtain

$$I_3' = 3a$$
$$I' = x - a \text{ and } (x - 2a)(x - a)/3a = 0{\cdot}00611 \ldots\ldots \text{(I).}$$
$$I_2 = x - 2a,$$

where $x = (4{\cdot}5 - 8{\cdot}37/5{\cdot}15)10^{-2}$ gm.-atom per litre
$= 2{\cdot}875 \times 10^{-2}$ gm.-atom per litre.

Inserting this value of x in (I) and solving for a, we obtain

$$a = 0{\cdot}58 \times 10^{-2} \text{ gm.-atom per litre.}$$

Hence $(I') = \{2{\cdot}875 - 0{\cdot}58\} \times 10^{-2} = 2{\cdot}30 \times 10^{-2}$ gm.-atom per litre.

Hence $K_{25^\circ} = \dfrac{(1{\cdot}625 \times 10^{-2})(1{\cdot}625 \times 10^{-2})^{\frac{1}{2}}}{(0{\cdot}380 \times 10^{-2})(2{\cdot}30 \times 10^{-2})} = 23{\cdot}6,$

a value in close agreement with that of Brönsted and Pedersen.

The slight discrepancy between 23·6 and 21·1 for the values of K in the two investigations is probably accounted for by the fact that Brönsted and Pedersen utilised only chlorides and iodides of iron and potassium whilst in the present case ammonium sulphate was present in addition.

Summary.

The reaction $2Fe^{\cdot\cdot\cdot} + I_2 \rightleftarrows 2Fe^{\cdot\cdot} + 2I'$ is photosensitive to both ultra-violet and visible light. The region of visible photoactive radiation is within the range 5500—6500 Å. with an apparent

maximum at 5800 Å. The tri-iodide ion is the photoactive constituent, and the energy of excitation corresponding to a wave-length 5800 Å. is equivalent to 2·14 volts, a value almost identical with the resonance potential of the iodine molecule. It is found that one quantum of absorbed radiant energy causes 1 mol. of iodine to react; the mechanism of the reaction can be expressed in the form $2\overbrace{FeI_2 + I_3'} + h\nu = 2FeI_3 + I'$.

The dark equilibrium constant of the reaction is

$$K = 23{\cdot}6 = (Fe^{\cdots})(I_2)^{\frac{1}{2}}/(Fe^{\cdots})(I') \text{ at } 25°.$$

The temperature coefficient of the liberation of iodine in the dark is $k_{35°}/k_{25°} = 2{\cdot}713$, whilst that of the photochemical reaction is $k'_{35°}/k'_{25°} = 1{\cdot}17$. The addition of potassium chloride raises the thermodynamic concentrations of all the reactants and, although the equilibrium point is unchanged, the rate of attainment is very considerably increased.

Proof is given that equilibrium is the result of attainment of equal velocities of the forward and the back reaction, since the effect of radiation of constant intensity on the equilibrium attained is less when the thermodynamic concentrations of the reactants (and thus the reaction velocities of the two reactions) are raised by the addition of potassium chloride.

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XLIV.—*The Condensation of Phenylethylamine with s-Dichlorodimethyl Ether.*

By WALLACE FRANK SHORT.

By the action of β-phenylethylamine on an excess of methylal in presence of concentrated hydrochloric acid at 100°, Pictet and Spengler (*Ber.*, 1911, **44**, 2030) obtained tetrahydro*iso*quinoline in 36% yield. By a similar method, Pictet and Gams (*Ber.*, 1911, **44**, 2629) prepared hydronorhydrastinine from homopiperonylamine, but Decker and Becker (*Ber.*, 1912, **45**, 2404), who repeated the experiments, obtained a base of the type $NHR{\cdot}CH_2{\cdot}NHR$. Phenylethylamine itself yielded β-phenylethyldimethylamine when condensed with an excess of formalin at 130—140°. The same

authors have shown (*Annalen*, 1913, **395**, 342) that homopiperonylamine and other derivatives of β-phenylethylamine react readily at room temperature with an equimolecular quantity of an aldehyde to form the alkylidene derivative, which is converted into a tetrahydro*iso*quinoline derivative by a suitable catalyst.

Rosenmund (*Ber. Deut. pharm. Ges.*, 1919, **29**, 200) condensed homopiperonylamine (2 mols.) with *s*-dichlorodimethyl ether (1 mol.) in ethereal solution and obtained homopiperonylaminomethanol as a very unstable oil, which was converted almost quantitatively into hydronorhydrastinine by heating at 100° with 10% hydrochloric acid.

In view of the above results, it appeared to be of interest to determine whether a good yield of tetrahydro*iso*quinoline could be obtained by the condensation of β-phenylethylamine with the so-called "chloromethyl alcohol." The products of the reaction were tetrahydro*iso*quinoline (yield 59%), *di*(β-*phenylethylamino*)-*methane*, and bases of unknown constitution.

Experimental.

β-Phenylethylamine was obtained in 30% yield (Wohl and Berthold, *Ber.*, 1910, **43**, 2183). *s*-Dichlorodimethyl ether was prepared by Stephen, Short, and Gladding's method (J., 1920, **117**, 513).

A mixture of 31·5 g. (2 mols.) of β-phenylethylamine hydrochloride, 14·4 g. of *s*-dichlorodimethyl ether (1½ mols., equivalent to 2½ mols. of chloromethyl alcohol), 0·5 g. of anhydrous zinc chloride, and 100 c.c. of dry ether was cooled to room temperature, stirred for ½ hour, and heated for 4 hours on the water-bath. Distillation in a vacuum left a brown syrup, which was dissolved in water, the solution made alkaline, and extracted with ether. The oily residue from the ethereal extract on solution in dilute hydrochloric acid and treatment with sodium nitrite gave a yellow oil, which, on reduction with tin and concentrated hydrochloric acid, deposited β-phenylethyl chloride. The aqueous layer was extracted with ether, made alkaline with caustic soda, and again extracted with ether. The second extract was distilled up to 235°, and the distillate converted into a picrate which, crystallised thrice from alcohol, melted at 196°; the base generated therefrom by addition of ammonia had b. p. 234°/763 mm. (yield 15·7 g.) (Found: C = 81·10; H = 8·39. Calc. for $C_9H_{11}N$, C = 81·15; H = 8·33%). These constants are in good agreement with those given in the literature for tetrahydro*iso*quinoline, and show that the product cannot be Becker and Decker's β-phenylethyldimethylamine.

The residue in the distilling flask was dissolved in hydrochloric acid, boiled with animal charcoal, and recrystallised several times

from water. The colourless crystals so obtained did not melt at 300°. The base, liberated with caustic soda, consisted of white needles of *di*(β-*phenylethylamino*)*methane*, m. p. 153°, and absorbed carbon dioxide from the air (Found: C = 80·16; H = 8·73; N = 10·82. $C_{17}H_{22}N_2$ requires C = 80·25; H = 8·72; N = 11·02%). About 10% of the β-phenylethylamine is converted into this secondary diamine. The *diacetyl* derivative forms silky needles, m. p. 191°.

My thanks are due to Mr. F. H. V. Fielder, B.Sc., for assistance in preparing the β-phenylethylamine for this investigation.

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XLV.—*New Halogen Derivatives of Camphor. Part VI. β-Bromocamphor-α-sulphonic Acid. Part VII. The Constitution of the Reychler Series of Camphorsulphonic Acids. Experiments on Chlorosulphoxides.*

By HENRY BURGESS and THOMAS MARTIN LOWRY.

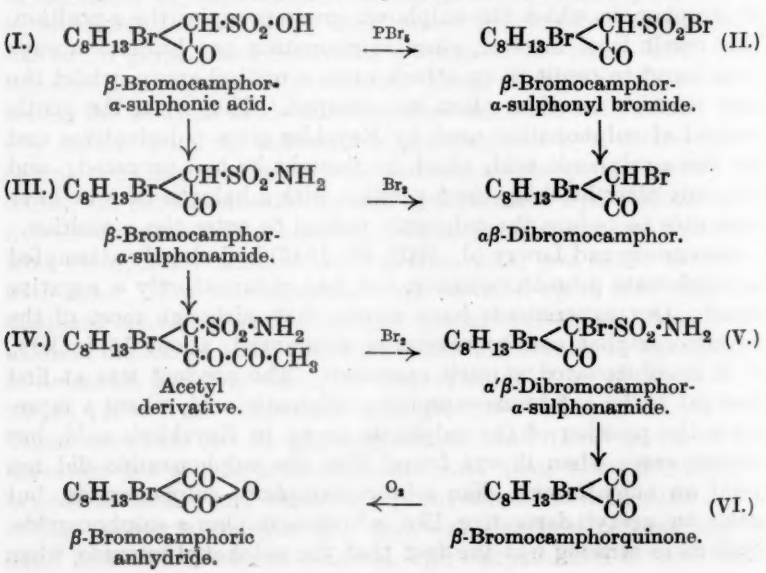
Part VI.—β-*Bromocamphor-α-sulphonic Acid.*

THE present paper describes a new series of sulphonic derivatives of camphor, in which the sulphonic group occupies the α-position. This result is of interest, since sulphonation has hitherto always been found to result in an attack upon a methyl group, whilst the very reactive α-carbon atom has escaped. Thus even the gentle method of sulphonation used by Reychler gives β-derivatives and not the α-sulphonic acid, which he thought he had prepared; and it is only after blocking the β-position with a halogen that we have been able to induce the sulphonic radical to enter the α-position.

Armstrong and Lowry (J., 1902, **81**, 1445) had already attempted to sulphonate β-bromocamphor, but had obtained only a negative result. Our experiments have shown that, although most of the β-bromocamphor can be recovered unchanged, about 15 to 20% of it is sulphonated at each operation. The product was at first thought to be a β-bromocamphor-ρ-sulphonic acid, where ρ represents the position of the sulphonic group in Reychler's acid, but doubts arose when it was found that the sulphonamide did not yield an anhydramide, like α-bromocamphor-ρ-sulphonamide, but gave an acetyl derivative like α-bromocamphor-π-sulphonamide. Still more striking was the fact that the sulphonyl bromide, when

decomposed by heat, did not give a new βρ-dibromocamphor, but a mixture of Kachler and Spitzer's αβ-dibromocamphor with our new α′β-dibromocamphor (J., 1923, **123**, 1867). This suggested that the sulphonic group occupied the α-position; but as the whole research was based upon a suspicion that the pyrogenic decomposition of a ρ-sulphonyl bromide might give a β-bromo-compound of different orientation, we did not regard it as safe to accept the above observation as a final proof of the structure of the acid. Confirmation was, however, obtained when the sulphonamide on bromination again gave rise to the same αβ-dibromocamphor, by a remarkable action in which *the halogen displaces a sulphonamide group* instead of eliminating one of the reactive α-hydrogen atoms. This result was very difficult to explain unless the sulphonic group were already in the α-position. Moreover, this bromination was free from the suspicions which attached to the formation of αβ-dibromocamphor by the pyrogenic decomposition of the sulphonyl bromide. Final proof that the sulphonic group had entered the α-position, leaving the camphor nucleus intact except for the presence of the β-bromine atom, was obtained when the spontaneous oxidation of a dibromosulphonamide derived from our acid gave rise to the hitherto unknown β-*bromocamphorquinone*, and thence by a direct further oxidation to β-*bromocamphoric anhydride* (not the free acid, although the oxidation took place in aqueous solution).

The whole series of actions may be set out as follows:



In these formulæ the acetyl derivative has been assumed to be enolic, as in the case of the π-isomeride, the solubility of which (unlike that of the amide from which it is derived) is not increased by the addition of alkali (Lowry and Magson, J., 1906, **89**, 1044), so that the acetyl derivative appears not to contain an α-hydrogen atom. In the present case, the fact that the acetyl group was lost on bromination suggested very strongly that we were again dealing with an enolic acetate and not the $-SO_2\cdot NHAc$ compound.

This investigation confirms the view of Lipp and Lausberg (*Annalen*, 1924, **436**, 274) that *β-bromocamphor and the Reychler series of camphorsulphonic acids have the same orientation*, since the blocking of the β-position by a halogen compels the sulphonic group to enter a new position in the molecule. The question whether the β-substituents are attached to a carbon atom in the ring, or to a methyl group is discussed in Part VII below.

Experimental.

Sulphonation of β-Bromocamphor.—β-Bromocamphor (50 g.) was added slowly to a mixture of acetic anhydride (80 c.c.) and concentrated sulphuric acid (25 c.c.), when the mixture became brown and most of the β-bromocamphor dissolved. After standing for a week at 30—40°, it was heated for 2 hours and poured on to crushed ice, and the precipitated β-bromocamphor (41 g.) washed with water. Further heating, or varying the quantities of acetic anhydride and sulphuric acid, gave a smaller yield of sulphonate and a much larger quantity of brown charred material. The solution was boiled till free from acetic acid, neutralised with a cream of calcium carbonate, filtered, and concentrated. The sludge of chalk and calcium sulphate (which separates only slowly in the presence of the calcium sulphonate) was washed three times with boiling water to remove all the sulphonate. After recrystallising three times from methylated spirit, the calcium sulphonate was obtained in colourless, rhombic plates. The mother-liquors were decolorised by bone charcoal. The total yield was 12 g. (about 90%) after allowing for the recovery of most of the bromocamphor. 0·1515 gave 0·1800 of CO_2, 0·0660 of H_2O, and 0·0273 of $CaSO_4$. 0·1773 lost 0·0172 of H_2O, and gave 0·0924 of AgBr: C = 32·41, H = 4·87, Ca = 5·30, Br = 22·18, H_2O = 9·70. $(C_{10}H_{14}OBr\cdot SO_3)_2Ca,4H_2O$ requires C = 32·78, H = 4·95, Ca = 5·47, Br = 21·83, H_2O = 9·84%.

Calcium β-bromocamphor-α-sulphonate is very soluble in hot water, but crystallises readily from hot methylated spirit. It does not melt below 250°. It has $[\alpha]_{5780} = +50°$, $[\alpha]_{5461} = +59°$, $[\alpha]_{4358} = +116{\cdot}5°$ in water (2 g. per 100 c.c.).

Potassium β-bromocamphor-α-sulphonate, prepared by addition of potassium oxalate (calc. amt.) to a solution of the calcium salt, filtration, and evaporation, crystallised from hot methyl alcohol in fine, colourless needles. 0·2045 gave 0·2565 of CO_2 and 0·0730 of H_2O. 0·2152 lost no water at 150—160° in a vacuum: C = 34·22, H = 4·00. $C_{10}H_{14}OBr{\cdot}SO_3K$ requires C = 34·37, H = 4·04%.

β-Bromocamphor-α-sulphonyl Chloride (Formula as II).—A mixture of powdered phosphorus pentachloride (5·4 g.) and the dry, powdered potassium salt (7·5 g.) was shaken and warmed in a dry flask on the water-bath, until liquid. After 15 minutes, it was shaken vigorously with powdered ice. The light brown solid was filtered, and washed with water and a little dilute potassium carbonate solution; it crystallised from ether in large, compact crystals (Fig. 1), which softened at 93° and melted at 97°. 0·2393

FIG. 1.

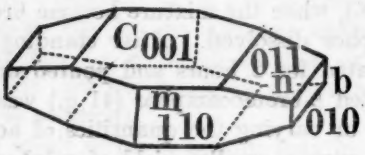
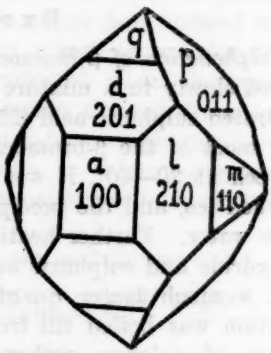


FIG. 2.



gave 0·0940 of AgCl: Cl = 9·7. $C_{10}H_{14}OBr{\cdot}SO_2Cl$ requires Cl = 10·76%.

β-Bromocamphor-α-sulphonyl chloride is comparatively stable when pure, but loses chlorine quickly if impure, and especially in presence of a little hydrochloric acid. It is very soluble in benzene or ether, less soluble in cold alcohol, and sparingly soluble in light petroleum.

The crystallographic properties are as follows (two crystals were measured):

System: Orthorhombic.

Axial Ratios: $a : b : c = 0{\cdot}2994 : 1 : 0{\cdot}3769$.

Habit: Both crystals were flattened parallel to *C*(001), with *m*(110) fairly large. The crystals were not quite transparent, and did not give good reflections.

Forms present: *C*(001), *b*(010), *m*(110), and *n*(011). One face only of *y*(021).

Angles observed.	No. of measurements.	Limits.	Mean observation.	Calculation.
bm 010 : 110	8	69° 52′—68° 59′	69° 21′	—
cn 001 : 011	8	17 1½—16 30	16 40	—
cy 001 : 021	1	30 25½—31 35½	31 0½	30° 55′
mn 110 : 011	4	84 28 —84 2	84 11	84 12

Optical Characters: Since the crystals could not be immersed in liquids, the optical data are scanty, and liable to be inaccurate. The optic axial plane is parallel to *b*(010), with the acute bisectrix perpendicular to *C*(001), and the double refraction positive. The refractive indices determined by the minimum deviation method are very approximately $\alpha = 1{\cdot}55$, $\beta = 1{\cdot}56$, $\gamma = 1{\cdot}58$.

β-*Bromocamphor-α-sulphonamide* (Formula III).—A mixture of the potassium sulphonate (7·0 g.) and phosphorus pentachloride (4·2 g.) was covered with dry chloroform (50 c.c.) and left overnight. The chloroform was washed twice with ice-cold water, dried for an hour over calcium chloride, filtered, and excess of dry ammonia was passed into it, when much heat was developed. After 12 hours, the chloroform was distilled off, and the residue was washed with water and crystallised from ether (yield 65%). 0·2045 gave 0·2895 of CO_2 and 0·0955 of H_2O. 0·2268 gave 0·1382 of AgBr: C = 38·62, H = 5·23, Br = 25·93. $C_{10}H_{16}O_3NBrS$ requires C = 38·71, H = 5·20, Br = 25·77%.

β-Bromocamphor-α-sulphonamide is very soluble in chloroform, alcohol, ether, or hot benzene, less soluble in cold benzene, and sparingly soluble in light petroleum or water. It melts at 100—102°, with the evolution of small bubbles of gas, and has $[\alpha]_{5780}$ + 39·3°, $[\alpha]_{5461}$ + 46·1°, $[\alpha]_{4358}$ + 99° in alcohol (5·62 g. per 100 c.c.).

The crystals which separate from an ethereal solution are tough and fibrous when crushed, they are at first quite transparent, but after about 2 hours the surface becomes opaque, and then the whole of the crystal, perhaps as a result of polymorphic change. When this change is complete, the crystal is easily crushed, the fibrous structure having been lost completely.

Attempts to Prepare an Anhydramide.—Lowry's two methods (J., 1902, **81**, 1441) were employed.

(*a*) A mixture of the sulphonamide (0·5 g.) with 45 c.c. of concentrated hydrochloric acid was kept for a fortnight, the clear solution diluted with water (2 vols.), and neutralised with potassium carbonate. Chloroform extracted the sulphonamide unchanged.

(*b*) The sulphonamide (2·5 g.) was heated with acetic anhydride (10 c.c.) on the water-bath for 4 hours,* crystals separating. After

* If the mixture is boiled, instead of being heated on a water-bath, considerable charring occurs.

cooling, these were filtered off and a further small quantity was obtained by diluting the cold mother-liquor with water (yield 80%). Although this product resembled α-bromocamphor-β-sulphonanhydramide in appearance and in its sparing solubility in all solvents, it was an *acetyl* derivative, for 0·2060 gave 0·3140 of CO_2 and 0·0955 of H_2O, and 0·1900 gave 0·1032 of AgBr and 0·1280 of $BaSO_4$: C = 41·58, H = 5·19, Br = 22·89, S = 9·25. $C_{10}H_{18}O_4NBrS$ requires C = 40·90, H = 5·15, Br = 22·69, S = 9·10%.

Acetyl-β-bromocamphor-α-sulphonamide (IV), prepared as described above, is slightly soluble in hot acetone, and in hot acetic anhydride, but is sparingly soluble in the cold solvents and in all the other common organic solvents. It crystallises from acetone in small, compact crystals, m. p. 217° (rapid decomp.). It has $[\alpha]_{5780} - 37{\cdot}5°$, $[\alpha]_{5461} - 42°$ in acetone (0·613 g. per 100 c.c.).

The crystallographic properties are as follows:

System: Orthorhombic.

Axial Ratios: $a : b : c = 1{\cdot}804 : 1 : 1{\cdot}206$.

Forms present: *a*(100), *m*(110), *l*(210), *q*(101), *d*(201), *p*(011).

Habit: The crystals were very small (Fig. 2), the longest dimension being about $\frac{1}{5}$". The faces were frequently curved and not well suited to accurate measurement. The face *a*(100) was only observed on two crystals. The prism faces were always very small, with the domes predominating, to give a stumpy outline.

Angles observed.	No. of measurements.	Limits.	Average.	Calculated.
$mm' = 110 : \bar{1}10$	5	57° 29′— 59° 51′	58° 43′	58° 0′
$ll' = 210 : 2\bar{1}0$	5	84 22 — 86 16	85 32	84 6
$pp' = 011 : 0\bar{1}1$	6	99 58 —102 24	101 0	100 40
$qq' = 101 : \bar{1}01$	6	67 54 — 70 23	68 50	67 32
$dd' = 201 : 20\bar{1}$	6	73 0 — 75 19	74 9	73 34
$mq = 110 : 101$	6	71 22 — 73 49	73 13	74 22
$mp = 110 : 011$	5	46 53 — 48 31	47 52	47 41
$ld = 210 : 201$	10	53 51 — 56 19	54 18	53 30
$lp = 210 : 011$	10	56 34 — 59 25	57 43	58 58
$lq = 210 : 101$	4	65 13 — 65 41	65 26	65 37
$md = 110 : 201$	2	66 41 — 68 44	67 24	67 9

Cleavage: None observed.

Specific gravity: 1·562 determined by floating in Thoulet's solution.

Decomposition of β-Bromocamphor-α-sulphonyl Bromide (Formula II).—The method of preparation was similar to that used in making the sulphonyl chloride. As the oil obtained on evaporating off the chloroform from the washed and dried solution did not crystallise in a desiccator in 2 days, it was dissolved in dry xylene and refluxed for about ½ hour until the evolution of sulphur dioxide, which

was at first very rapid, had practically ceased. The liquid charred rather badly during the heating. After the xylene had been distilled off in steam, a colourless oil came over and slowly solidified. This was filtered off, and melted at 46—85°. When crystallised from dilute alcohol, it gave three successive crops of crystals. The first fraction, which melted almost constantly at 92—94°, on three successive crystallisations, was at once converted into almost pure αβ-dibromocamphor on crystallising in presence of a trace of piperidine, and therefore was a mixture of αβ- and α′β-dibromocamphors (compare J., 1923, **123**, 1872). The second fraction, after one further crystallisation, was identified as α′β-dibromocamphor (m. p. 133—135°, not lowered by mixing; $[\alpha]_{5461}$ − 77° instead of − 85° in acetone, 1 g. per 100 c.c.). The third fraction was identified, after one further crystallisation, as αβ-dibromocamphor (m. p. 113—114°, not lowered by mixing with αβ-dibromocamphor; $[\alpha]_{5461}$ 125° instead of 127° in acetone, 3·92 g. per 100 c.c.). The above results proved quite conclusively that the sulphonyl bromide had decomposed to a mixture of αβ- and α′β-dibromocamphors.

Bromination of β-*Bromocamphor-*α-*sulphonamide.*—Bromine (2·7 g.) was added to a solution of the sulphonamide (2·0 g.) in glacial acetic (50 c.c.), and the mixture refluxed for 4 hours, becoming pale yellow. From the aqueous solution, neutralised with sodium carbonate, ether extracted an oil (about 2 c.c.), containing some lachrymatory substance, probably bromoacetic acid, from which was separated about 0·3 g. of αβ-dibromocamphor, m. p. 112—114° (alone or mixed with this substance).

α′β-*Dibromocamphor-*α-*sulphonamide* (Formula V).—Bromine (2·5 g.) was added to the acetyl derivative of β-bromocamphor-α-sulphonamide (0·8 g.) in glacial acetic acid (20 c.c.), and the mixture refluxed for 5 hours, the acetyl derivative dissolving completely, and the bromine disappearing. After cooling, the acetic acid was neutralised with ammonia, the mixture being cooled meanwhile; the white precipitate crystallised from benzene–ligroin in beautiful, colourless prisms, m. p. 145°, softening at 143° (yield 0·7 g., or 80%). 0·2015 gave 0·2310 of CO_2 and 0·0710 of water. 0·1818 gave 0·1751 of AgBr and 0·1070 of $BaSO_4$: C = 31·27, H = 3·94, Br = 40·99, S = 8·08. $C_{10}H_{15}O_3NBr_2S$ requires C = 30·86, H = 3·89, Br = 41·08, S = 8·24%).

α′β-Dibromocamphor-α-sulphonamide is insoluble in water, sparingly soluble in light petroleum, but very soluble in other organic solvents. It has $[\alpha]_{5780}$ − 26°, $[\alpha]_{5461}$ − 29° in benzene (2·64 g. per 100 c.c.). When warmed with aqueous sodium hydroxide, it liberates ammonia.

β-*Bromocamphorquinone* (Formula VI).—During a crystallisation

of dibromocamphorsulphonamide from dilute alcohol the solution slowly became yellow, and deposited bright yellow crystals as well as the colourless ones of the initial compound. After a week, a large proportion of the colourless crystals had disappeared, whilst the yellow compound had increased in quantity. The mixture was filtered off and sublimed in a vacuum, when bright yellow prisms, m. p. 104—107°, were obtained. These were recrystallised from dilute alcohol and melted at 122° after softening above 115°. 0·04766 gave 0·03655 of AgBr (micro-Carius): Br = 32·63. $C_{10}H_{13}O_2Br$ requires Br = 32·61%.

Attempts to prepare it by hydrolysis with sodium ethoxide and with calcium hydroxide failed; both gave the intense colour of the quinone, but very little could be separated. Oxidation with hydrogen peroxide in aqueous alcoholic solution first gave the intense yellow colour of the quinone; but further heating led to its decomposition, with the formation of β-bromocamphoric anhydride, m. p. about 143° (alone or mixed with a genuine specimen); the rotatory power (+ 7°) also was in harmony with that (+ 5°) of a specimen of the anhydride prepared from β-bromocamphoric acid. The yellow colour also disappears slowly by oxidation when the quinone is left in contact with aqueous alcohol.

β-Bromocamphorquinone is very soluble in benzene, ether, or chloroform, less soluble in alcohol, and insoluble in water. It has a characteristic pleasant odour which is unlike that of camphorquinone. The absorption spectrum in alcoholic solution of a specimen melting at 104—107° gave an absorption band at the same wave-length as that of camphorquinone. The results are given in Table I.

TABLE I.

The Absorption of β-Bromocamphorquinone in Alcohol.

Conc. of solution = 0·0993 g.-mol. per litre. Length of tube = 1 dcm.

λ.	4300.	4400.	4500.	4550.	4600.	4650.	4700.	4750.
log ϵ_1	0·891	1·012	1·127	1·147	1·158	1·160	1·149	1·145
log ϵ_2	1·15	1·32	1·41	1·458	1·460	1·462	1·460	1·457
λ.	4800.	4850.	4900.	5000.	5100.	5200.	5300.	
log ϵ_1	1·120	1·010	0·790	0·261	$\bar{1}$·947	$\bar{1}$·735	$\bar{1}$·626	
log ϵ_2	1·425	1·365	1·230	0·528	0·085	$\bar{1}$·442	—	

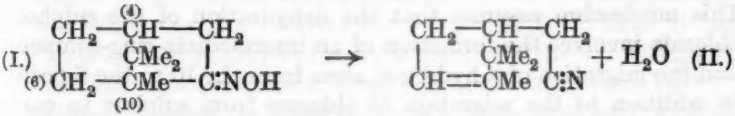
ϵ_1 is the extinction coefficient for β-bromocamphorquinone.

ϵ_2 is the extinction coefficient for camphorquinone (Lowry and French, J., 1924, **125**, 1921).

We are indebted to Mr. R. Jeffery of Peterhouse, for the crystallographic measurements, which he obtained under the direction of Mr. A. Hutchinson, F.R.S.

Part VII.—*The Constitution of the Reychler Series of Camphorsulphonic Acids. Experiments on Chlorosulphoxides.*

The position occupied by the sulphonic group in Reychler's camphorsulphonic acid, and the related question of the position of the halogen in β-bromocamphor, have recently come up for reconsideration, since Wedekind, Schenk, and Stusser (*Ber.*, 1923, 56, 633) have discovered a series of reactions by which Reychler's acid can be converted into ketopinic acid by the destruction of one of the methyl groups of the original molecule of camphor. The evidence thus supplied that the sulphonic radical has entered a *methyl* group is, however, at variance with the equally definite evidence that the halogen of β-bromocamphor (which can be prepared by the thermal decomposition of the sulphonyl bromide of Reychler's acid) has entered a *methylene* group in the ring. Part of this evidence was reviewed by Armstrong and Lowry (J., 1902, 81, 1469), who directed attention to the oxidation of β-bromocamphor to β-bromocamphoric acid, but were unable to oxidise it further to a tricarboxylic acid, and by M. O. Forster (J., 1902, 81, 265), who directed attention to the ready conversion of β-bromocamphor into campholenic acid (compare Part V, J., 1924, **125**, 2376): but further results have since become available which point in the same direction. Thus not only is campholenonitrile (II) readily formed by the removal of water from camphoroxime (I),

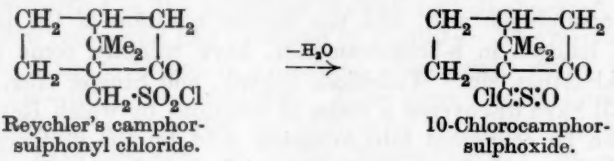


but a similar action takes place in the case of epicamphoroxime, where the methyl group has been transplanted bodily to the 4-position. It is therefore remarkable that this action does not occur in β-bromocamphoroxime, if, as is now suggested, the β-bromine which inhibits the action is in the inactive methyl group, instead of in the methylene group from which the hydrogen of the eliminated molecule of water is taken.

The two lines of evidence disagree so much that it appeared impossible to reconcile them unless (i) a migration of the bromine atom had occurred in the preparation of β-bromocamphor from the sulphonyl bromide of Reychler's acid, or (ii) some change of orientation had taken place during the conversion of the sulphonyl chloride of Reychler's acid into ketopinic acid. The first hypothesis is negatived by the results recorded in Part VI above; the present part deals with the second hypothesis.

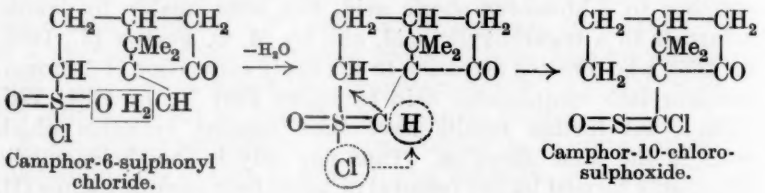
As a first step in the conversion of Reychler's camphorsulphonyl

chloride to ketopinic acid, Wedekind and his colleagues obtained by loss of water a chlorocamphorsulphoxide which they formulated as follows:



Reychler's camphorsulphonyl chloride. 10-Chlorocamphorsulphoxide.

Since they obtained a similar compound from camphor-π-sulphonyl chloride, but not from aromatic sulphonylchlorides, they concluded that *chlorosulphoxides can be obtained only from acids in which a methyl group has been sulphonated.* An alternative view, which would explain the formation of 10-ketopinic acid from a 6-derivative of camphor, postulates instead that a *methyl group must be contiguous to the sulphonic radical,* thus:



Camphor-6-sulphonyl chloride. Camphor-10-chlorosulphoxide.

This mechanism assumes that the dehydration of the sulphonylchloride involves the formation of an intermediate ring-compound, and the migration of a hydrogen atom from the 10 to the 6-position in addition to the migration of chlorine from sulphur to carbon which was postulated by Wedekind, Schenk, and Stusser.

This mechanism appeared all the more plausible because in camphor-π-sulphonyl chloride there is a methyl group in a precisely similar position relative to the sulphonic radical, since both compounds contain the group $\begin{matrix}>C\cdot SO_2Cl\\ >C\cdot CH_3\end{matrix}$. In the case of the π-compound, however, it was possible to determine whether a change of orientation had occurred in the dehydration of the sulphonyl chloride, since a different methyl group would then be destroyed on converting into a carboxylic acid (i) the π-bromocamphor obtained by the pyrogenic decomposition of camphor-π-sulphonyl bromide (presumably without change of orientation, compare Part VI above); (ii) the π-chlorosulphoxide obtained by dehydration of the π-sulphonyl chloride by Wedekind's method. If this wandering took place, therefore, the tricarboxylic acid obtained by oxidising Wedekind's *iso*ketopinic acid should be isomeric and not identical

with the acid which Kipping and Pope obtained by hydrolysing and then oxidising π-bromocamphor.

Since Wedekind and his collaborators did not mention whether they had oxidised their product to a tricarboxylic acid, we decided to test the reaction by preparing and oxidising (instead of their compound) an α-bromocamphor-π-chlorosulphoxide prepared from ammonium α-bromocamphor-π-sulphonate. When this was oxidised with nitric acid, a tricarboxylic acid and anhydride were obtained, which were identical and not isomeric with those prepared by Kipping and Pope. There was therefore no evidence here of a change of orientation.

We also attempted to prepare chlorotoluenesulphoxide from *o*-toluenesulphonyl chloride, since this compound also contains a methyl group in the appropriate position; but we were again unsuccessful, as most of the sulphonyl chloride was recovered unchanged. The evidence therefore undoubtedly proves that the suggested mechanism, which appeared to offer a feasible explanation of the production of 10-ketopinic acid from a camphor-6-sulphonic acid, is incorrect.

We have, then, no alternative but to accept the conclusion that the halogen in β-bromocamphor, as well as the sulphonic group in Reychler's acid, has entered a methyl group and occupies the 10-position in the camphor molecule. In doing so, however, it is desirable to point out that *there is no single reaction in which β-bromocamphor behaves as if it contains the group* $-CH_2Br$. Thus it has never been converted into a primary alcohol, $-CH_2Br \longrightarrow -CH_2{\cdot}OH$, and when attempts are made to bring about this change (see Part V), the molecule emerges (as a derivative of campholenic acid) with all its methyl groups intact, but with a double bond in the ring. On the other hand, it is amazing that a halogen in the side chain should absolutely inhibit the formation of this double bond in the ring, when the attempt is made to convert β-bromocamphoroxime into β-bromocampholenonitrile, especially in view of the fact that the side chain can be eliminated completely without affecting the action. The conclusion appears inevitable that there must be some link between the 6- and 10-positions which is not indicated by the conventional formulæ, just as there must be some connexion between the ketonic and the *gem*-dimethyl group (or some mechanism which involves both groups; see Armstrong and Lowry, J., 1902, **81**, 1409) to account for the π-sulphonation of camphor. The nature of this connexion is not yet clear, but it would be shirking the facts not to recognise that there is still a problem to solve, even when the admission has been made that the β-series of compounds are all 10-derivatives of camphor.

EXPERIMENTAL.

α-Bromocamphor-π-chlorosulphoxide, $C_9H_{12}BrO{\cdot}CCl{:}S{:}O$, was prepared by the method of Wedekind, Schenk, and Stusser (*loc. cit.*) from α-bromocamphor-π-sulphonyl chloride, using dry pyridine as the dehydrating agent; but twice as much pyridine was used because the reaction mixture went solid before the addition of the sulphonyl chloride was complete and the later portions did not then react. The brownish-red, granular solid was washed, and crystallised three times from acetone. 0·2003 gave 0·2830 of CO_2 and 0·0700 of H_2O. 0·1930 gave 0·2044 of AgCl + AgBr: C = 38·55, H = 3·91, Br = 25·56, Cl = 11·34. $C_{10}H_{12}O_2ClBrS$ requires C = 38·53, H = 3·88, Br = 25·65, Cl = 11·38%.

α-Bromocamphor-π-chlorosulphoxide is very soluble in benzene, hot acetone, or chloroform, less soluble in cold acetone and the alcohols, slightly soluble in hot ligroin or ether, and insoluble in water. It crystallises in thin plates which are usually pointed at one end, but are occasionally hexagonal in shape. Its colour varies from pale to deep reddish-brown according to the state of aggregation. It melts at 158—159° and has $[\alpha]_{5780}$ + 31°, $[\alpha]_{5461}$ + 39° in benzene (5·5 g. per 100 c.c.).

Oxidation of α-Bromocamphor-π-chlorosulphoxide.—This compound (3·5 g.) was refluxed with 20 c.c. of nitric acid (*d* 1·4) for 14 hours; the mixture was then cooled, and water was added. After extraction with benzene to remove an oily by-product, the aqueous layer was evaporated until crystals began to separate, and then cooled. The crystals, m. p. 180—185°, after filtration and washing with a little water, crystallised twice from benzene-chloroform and once from ether, gave a product which softened slightly at 193° and melted at 194—195° (decomp.); on mixture with a specimen of *trans*-camphotricarboxylic acid supplied by Prof. F. S. Kipping, F.R.S., its m.p. was undepressed. The substance had solubilities similar to those given by Kipping and Pope (J., 1896, 69, 951) for that acid, and gave precipitates with barium chloride, copper acetate, ferric chloride, and lead acetate as recorded by these authors. It has $[\alpha]_D$ + 34°, $[\alpha]_{5780}$ + 35°, and $[\alpha]_{5461}$ + 40° in alcohol (0·281 g. in 15 c.c.). The anhydride, prepared by heating with acetic anhydride, diluting with water, and extracting with ether, separated from the ether in beautiful plates, m. p. 252—254° (Pope and Kipping's *trans*-camphotricarboxylic acid melts at 195—196° [decomp.], has $[\alpha]_D$ + 37·2° in alcohol, and gives an anhydride, m. p. 253—254°).

The benzene extract gave a crystalline by-product, m. p. about 202° (decomp.), $[\alpha]_{5461}$ + 19·4° in acetone (2·166 g. per 100 c.c.).

This was expected to be a π-chlorodinitro-α-bromocamphor; but, unlike the compound which Wedekind obtained under analogous conditions, it was soluble in alkalis, as if it contained a primary or secondary, instead of only tertiary, nitro-groups. Moreover, it appeared to contain an additional molecule of water, although there was not enough material available to confirm the analysis. Since the constitution of the compound is still unknown, it is hoped to investigate it more fully later.

Attempt to Make Toluene-o-chlorosulphoxide.—*o*-Toluenesulphonyl chloride (14 c.c.) was heated with dry piperidine (11 g.) for 1½ hours, the liquid becoming of an intense dark red colour as in the case of α-bromocamphor-π-sulphonyl chloride. After washing with acidified water, extracting with ether, and drying over calcium chloride, the oil was distilled in a vacuum, 85% of the *o*-toluenesulphonyl chloride being recovered unchanged. The charred residue was not investigated.

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CAMBRIDGE. [*Received, November 18th*, 1924.]

XLVI.—*Conversion of Amino-acids into Tertiary Amino-alcohols.*

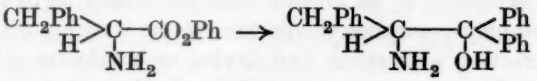
By ALEX. MCKENZIE and GEORGE OGILVIE WILLS.

THE first application of Grignard reagents towards esters of amino-acids was made by Baeyer and Villiger (*Ber.*, 1904, **37**, 3191), who converted methyl anthranilate into *o*-aminotriphenylcarbinol by means of magnesium phenyl bromide. Paal and Weidenkaff (*Ber.*, 1905, **38**, 1686) obtained β-amino-αα-diphenylethyl alcohol from ethyl glycine (compare also Paal and Weidenkaff, *Ber.*, 1906, **39**, 810, 4344; Krassusky, *Compt. rend.*, 1908, **146**, 236).

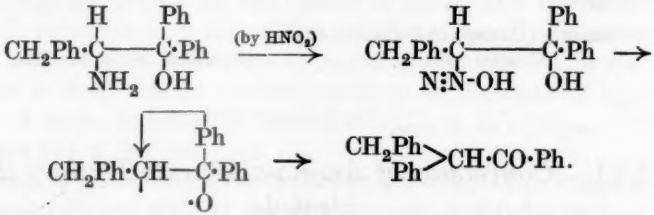
The Grignard reaction has been also applied in this laboratory for preparing amino-alcohols in connexion with the study of semi-pinacolinic deamination. Since other workers (Thomas and Bettzieche, *Z. physiol. Chem.*, 1924, **140**, 244, 261, 279; Bettzieche, *ibid.*, 273) have entered the same field quite recently, we think it desirable to describe our further results.

The elimination of the amino-group in tertiary amino-alcohols has been dealt with (McKenzie and Richardson, J., 1923, **123**, 79; McKenzie and Roger, J., 1924, **125**, 844; McKenzie and Dennler, J., 1924, **125**, 2105). The first instance described in the literature as a semipinacolinic deamination arose from the accidental discovery that the transformation $OH{\cdot}CPh_2{\cdot}CHPh{\cdot}NH_2 \rightarrow OH{\cdot}CPh_2{\cdot}CHPh{\cdot}OH$

could *not* be effected by the agency of nitrous acid; the product of the action was phenyldeoxybenzoin and *not* triphenylethylene glycol. β-Amino-ααβ-triphenylethyl alcohol was prepared by McKenzie and Barrow (J., 1913, **103**, 1331) by the action of magnesium phenyl bromide on *r*-desylamine hydrochloride and later on *r*-phenylaminoacetic acid by McKenzie and Richardson. Thomas and Bettzieche have repeated its preparation from phenylaminoacetic acid, and confirmed the conversion into phenyldeoxybenzoin. The conversion of *r*-phenylalanine into *r*-β-amino-β-benzyl-αα-diphenylethyl alcohol

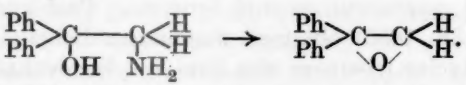


was also carried out in this laboratory and it was shown that the amino-alcohol undergoes semipinacolinic deamination:

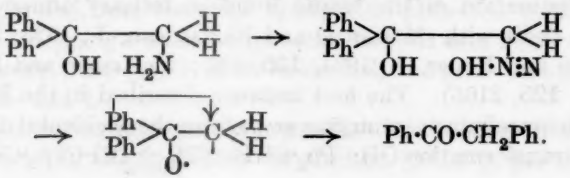


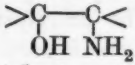
The phenyl group migrates, and the product is benzyldeoxybenzoin. Those results are also confirmed by Thomas and Bettzieche.

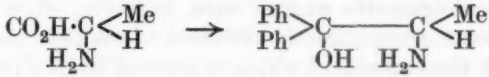
According to Paal and Weidenkaff (*loc. cit.*), the action of nitrous acid on β-amino-αα-diphenylethyl alcohol leads to the formation of *as*-diphenylethylene oxide:



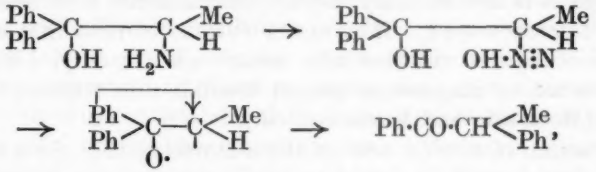
In the light of our work on semipinacolinic deamination, it seemed possible that this conclusion was erroneous, and that the product was actually deoxybenzoin. By arrangement with us, Professor Tiffeneau and M. Orékhov had kindly undertaken the investigation of this point, which meanwhile has been solved by Bettzieche. The product is deoxybenzoin, and we would interpret its formation on the following lines, the phenyl group migrating thus:



In a former paper, we mentioned that we were continuing our study of the action of nitrous acid on compounds containing the group  with the object of extending our experience ultimately to optically active amino-alcohols. Accordingly in the present paper we describe the action of magnesium phenyl bromide on *r*-alanine, thus :

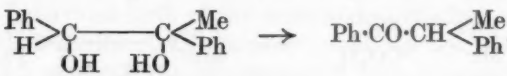


The amino-alcohol on deamination gave methyldeoxybenzoin :



and thus provided another instance of the striking regularity with which the phenyl group migrates in all the cases of semipinacolinic deamination which have been studied.

The change may be contrasted with the vinyl dehydration of *r*-methylhydrobenzoin studied by Tiffeneau and Orékhov (*Bull. Soc. chim.*, 1921, [iv], **29**, 422), and by McKenzie and Roger incidentally to their work on the dehydration of optically active methylhydrobenzoin by concentrated sulphuric acid :



The above result has already been arrived at by Bettzieche, who carried out the action with a trace of the amino-alcohol. In the light of the work of McKenzie and Roger as applied to the optically active methyl- and ethyl-hydrobenzoins, the extension of this action to the optically active amino-alcohol derived from *d*-alanine presents obvious points of interest, and we are at present engaged in the investigation of this topic.

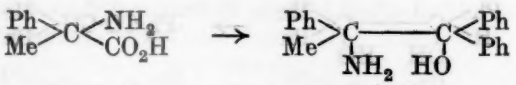
As already stated, the action of nitrous acid on β-amino-ααβ-triphenylethyl alcohol had been examined with the object of obtaining triphenylethylene glycol. The optically active forms of the latter compound had already been described (McKenzie and Wren, J., 1910, **97**, 473; McKenzie, Drew, and Martin, J., 1915, **107**, 26), and the change in question, if carried out with the optically active amino-alcohols, would have provided data in connexion with the Walden inversion. This scheme, however,

cannot be effected in practice for the reasons already given. Nevertheless, we have thought it desirable that the optically active amino-alcohols should at least be prepared. The description of their preparation is now given in the experimental part. The compounds in question are highly active, giving $[\alpha]_D \pm 243°$ in chloroform; they rotate the plane of polarisation in the opposite sense to the phenylaminoacetic acids from which they are prepared. There is no configurative change here, however, since there is no substitution of a group directly attached to the asymmetric carbon atom, so that the compound which is derived from *d*-phenylaminoacetic acid is designated as *d*-β-amino-ααβ-triphenylethyl alcohol, although it is lævorotatory, *d*-phenylaminoacetic acid being taken as the reference type. It is rather curious to note that a similar change of sign of rotation also occurs when methyl *l*-mandelate is converted by magnesium phenyl bromide into triphenylethylene glycol (McKenzie and Wren, *loc. cit.*).

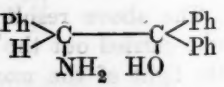
The action of nitrous acid on the *d*-amino-alcohol gives an optically inactive product owing to semipinacolinic deamination, the product being phenyldeoxybenzoin.

The isomeric camphorsulphonates of the *d*- and *l*-amino-alcohols were prepared, but the resolution of the *r*-alcohol by *d*-camphor-β-sulphonic acid gave a very slow and imperfect separation, and the method was obviously unsatisfactory. We are at present engaged in resolving by means of camphorsulphonic acids the *r*-amino-alcohols related to desylamine.

The changes



and *d*-$CH_2Ph{\cdot}CH(NH_2){\cdot}CO_2H \rightarrow$ *d*-



are also described, but the study of the action of nitrous acid on the amino-alcohols has not yet been completed.

Arising from the present research, the following points have been investigated. The ethyl ester hydrochloride of *l*-phenylaminoacetic acid gives on hydrolysis with a slight excess of alcoholic potash a phenylaminoacetic acid with $[\alpha]_D - 12{\cdot}4°$ in hydrochloric acid solution, whereas the pure *l*-acid has $[\alpha]_D - 157{\cdot}8°$ in the same solvent. This result was anticipated, since in phenylaminoacetic acid we have both a phenyl group and a migrational hydrogen atom in direct attachment to the asymmetric carbon atom.

McKenzie and Walker (J., 1915, **107**, 1685) have shown that catalytic racemisation occurs when *l*-phenylbromoacetic acid is

acted on by ammonia. When the action was conducted in benzene solution, that portion of the bromo-acid which had survived the attack of the ammonia had become largely racemised. It was thought possible that something of the same kind might occur when *l*-phenylaminoacetic acid is acted on by nitrous acid; such, however, is not the case.

There was one other rather important point in connexion with the study of the Walden inversion in the mandelic acid series which clearly required elucidation. E. Fischer and Weichhold (*Ber.*, 1908, **41**, 1286) acted on ethyl *d*-phenylaminoacetate with nitrous acid and obtained *a change of sign* of rotation, the resulting ethyl mandelate being highly racemised, and lævorotatory. On the other hand, Marvel and Noyes (*J. Amer. Chem. Soc.*, 1920, **42**, 2259), by acting on a solution of the hydrochloride of ethyl *l*-phenylaminoacetate in dilute sulphuric acid with nitrous acid, obtained an ethyl mandelate of *the same sign* of rotation as that of the original ethyl *l*-phenylaminoacetate. We have repeated the work both of Fischer and Weichhold and of Marvel and Noyes, and have found that a change of sign of rotation occurs when ethyl *l*-phenylaminoacetate is acted on by nitrous acid if the solution, before the ester is extracted, is kept sufficiently long after the addition of the nitrite. Fischer and Weichhold's conclusion,

$$d\text{-CHPh(NH}_2\text{)}\cdot\text{CO}_2\text{Et} \longrightarrow l\text{-CHPh(OH)}\cdot\text{CO}_2\text{Et},$$

is therefore correct. Since McKenzie and Clough (J., 1909, **95**, 777) have shown that the change

$$d\text{-CHPh(NH}_2\text{)}\cdot\text{CO}_2\text{H} \longrightarrow l\text{-CHPh(OH)}\cdot\text{CO}_2\text{H}$$

occurs, the behaviour both of the ester and of the free acid towards nitrous acid is similar. The product obtained by the method of the American workers was contaminated with a nitrogenous compound (probably a diazo-compound). It seems that they had proceeded to isolate their ethyl mandelate too quickly after the addition of the sodium nitrite.

The work on the action of nitrous acid on compounds containing the grouping $>\overset{\text{OH}}{\text{C}}-\overset{\text{NH}_2}{\text{C}}<$ is being continued.

Experimental.

Semipinacolinic Deamination of β-*Amino-*αα*-diphenyl*-n-*propyl Alcohol.*—Ethyl *r*-alanine hydrochloride (compare Curtius and Koch, *J. pr. Chem.*, 1888, [ii], **38**, 472; Barker and Skinner, *J. Amer. Chem. Soc.*, 1924, **46**, 403) was conveniently prepared as follows: A current of dry hydrogen chloride was passed into a suspension of *r*-alanine (10 g.) in ethyl alcohol (200 c.c.) for 1 hour, and the mixture, after boiling for 1 hour longer, was evaporated

to dryness at the ordinary temperature under 15 mm. pressure. The resulting syrup solidified when kept over soda–lime in a vacuum. It crystallised from ethyl acetate in needles (15·5 g.; 90% of the theoretical). Ethyl *r*-alanine hydrochloride (20 g.) was added gradually to the Grignard reagent prepared from bromobenzene (245 g.), and the mixture heated for 8 hours. The product was decomposed by ice, ammonium chloride and ammonia. The residual solid was extracted with ether and added to the main ethereal solution. After removal of ether and diphenyl as usual, the product (20 g.) was dissolved in hydrochloric acid and precipitated by ammonia. This treatment was repeated and then the product was crystallised three times from aqueous alcohol.

β-*Amino-αα-diphenyl*-n-*propyl alcohol* separates from aqueous alcohol in rhombohedral plates, m. p. 101·5—102·5°, is readily soluble in ethyl alcohol, methyl alcohol, benzene, toluene, carbon tetrachloride, carbon disulphide, acetone, or ether, and very sparingly soluble in water (Found: C = 79·4; H = 7·7; N = 6·2. $C_{15}H_{17}ON$ requires C = 79·3; H = 7·5; N = 6·2%). A trace added to concentrated sulphuric acid assumes a golden-yellow tint, and the solution becomes at first pink and quickly colourless.

A solution of 4·5 g. of sodium nitrite in 20 c.c. of water was gradually added (¾ hour) to a solution of 5 g. of the amino-alcohol in 150 c.c. of 25% acetic acid, cooled at 0°. A flocculent precipitate was gradually deposited, which was filtered off after 24 hours, and crystallised from aqueous alcohol. The silky needles (m. p. 50—51°) which separated amounted to 4 g., and were identified as methyldeoxybenzoin (Found: C = 85·8; H = 7·0. Calc., C = 85·7; H = 6·7%). There was no depression of the melting point when this substance was mixed with a specimen of the methyldeoxybenzoin prepared by McKenzie and Roger (J., 1924, **125**, 844) by the dehydration of methylhydrobenzoin with concentrated sulphuric acid. The coloration observed with concentrated sulphuric acid was identical with that described by McKenzie and Roger for their product. The identity of the substance was also proved by its behaviour towards magnesium phenyl bromide, when ααβ-triphenylpropyl alcohol, m. p. 86·5—87·5°, was isolated. The latter compound had already been prepared by Mlle Lévy (*Bull. Soc. chim.*, 1921, [iv], **29**, 878) and by McKenzie and Roger.

Hydrochlorides of Ethyl d- *and* l-*Phenylaminoacetates*.—The optically active phenylaminoacetic acids were prepared by E. Fischer and Weichhold (*Ber.*, 1908, **41**, 1286), who resolved the formyl *r*-acid by cinchonine and quinine and then hydrolysed the *d*- and *l*-formyl acids with hydrobromic acid. The resolution of

r-phenylaminoacetic acid into its optically active components by means of Reychler's *d*-camphor-β-sulphonic acid in aqueous solution has been described by Betti and Mayer (*Ber.*, 1908, **41**, 2071) and by Marvel and Noyes (*J. Amer. Chem. Soc.*, 1920, **42**, 2259), the acids being employed in equimolecular quantities. In the modification described by Ingersoll and Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 2930), an excess of the camphorsulphonic acid was used. Since the latter acid contains water of crystallisation (Pope and Gibson, J., 1910, **97**, 2211), and, since this may possibly be present in varying quantity, we employed this method. The optically pure *l*-acid was obtained by adding the requisite amount of ammonia to the solution of the salt obtained after several crystallisations. The *d*-acid may be prepared from the acid mixture obtained from the first mother-liquor of the preceding resolution either by means of *d*-α-bromocamphor-β-sulphonic acid or by formylating and then converting into the quinine salt. For the purification of the *d*-acid, however, it is more convenient to combine the crude acid with *l*-camphor-β-sulphonic acid, and then to crystallise until the camphorsulphonate is homogeneous. We were enabled to conduct the resolution in the latter manner owing to the generous gift of a supply of *l*-camphor from Sir William Pope. The *l*-camphorsulphonic acid, obtained from *l*-camphor by sulphonation in presence of acetic anhydride, was crystallised from ethyl acetate and gave in aqueous solution: $l = 2$, $c = 3{\cdot}8705$, $\alpha_D - 1{\cdot}61°$, $[\alpha]_D - 20{\cdot}8°$.

l-Camphorsulphonic acid combines with *l*-phenylaminoacetic acid to form a salt which is readily soluble in water, from which it separates in prisms. Its rotation was determined in aqueous solution: $l = 2$, $c = 4{\cdot}630$, $\alpha_D - 6{\cdot}64°$, $[\alpha]_D - 71{\cdot}7°$.

The diastereoisomeric salt, prepared from *d*-camphorsulphonic acid and *l*-phenylaminoacetic acid, has $[\alpha]_D - 44{\cdot}07°$ ($c = 2{\cdot}0885$, $l = 2$) in aqueous solution (Betti and Mayer, *loc. cit.*). This value enabled us to estimate the progress of the resolution of *r*-phenylaminoacetic acid by *d*- and *l*-camphorsulphonic acids. The polarimetric values for the *l*- and *d*-phenylaminoacetic acids obtained agreed with those of Fischer and Weichhold.

Ethyl l-*Phenylaminoacetate Hydrochloride.*—Fischer and Weichhold describe the conversion of *l*-phenylaminoacetic acid into the hydrochloride of its ethyl ester, which they describe as dextrorotatory, $[\alpha]_D^{20} + 88{\cdot}95°$ in aqueous solution ($p = 5{\cdot}021$, $d_4^{18} = 1{\cdot}0097$). Our results were different. For example, a current of dry hydrogen chloride was passed into a mixture of 3·3 g. of *l*-phenylaminoacetic acid and 40 c.c. of ethyl alcohol for 1½ hours. The solution was then boiled for a few minutes, and filtered from a

small amount of solid. The alcohol was removed from the filtrate by gentle warming under diminished pressure, the resulting acid dissolved in 20 c.c. of water, and an equal volume of benzene added. The addition of the requisite amount of ammonia caused the separation of the ester, which was extracted with benzene. A current of dry hydrogen chloride was passed into the benzene solution for 15 minutes, when the crystalline ester hydrochloride (4·2 g.) separated. It had the following rotation in aqueous solution: $l = 1$, $c = 5{\cdot}070$, $\alpha_D - 4{\cdot}53°$, $[\alpha]_D - 89{\cdot}3°$.

Marvel and Noyes also obtained a lævorotatory ester hydrochloride with $[\alpha]_D - 84{\cdot}6°$ (concentration not quoted) from the *l*-amino-acid. The dextrorotation recorded by Fischer and Weichhold is possibly due to a typographical error.

Ethyl d-*phenylaminoacetate hydrochloride* was prepared in a similar manner from *d*-phenylaminoacetic acid, 6·1 g. being obtained from 5·8 g. of *d*-acid. It was dextrorotatory in aqueous solution: $l = 1$, $c = 5{\cdot}070$, $\alpha_D + 4{\cdot}60°$, $[\alpha]_D + 90{\cdot}7°$.

Action of Magnesium Phenyl Bromide on the Hydrochlorides of Ethyl d- *and* l-*Phenylaminoacetate.*—The *d*-ester hydrochloride (6 g.; 1 mol.) was gradually added within 15 minutes to the Grignard reagent prepared from 52 g. of bromobenzene (12 mols.), 16·5 g. of magnesium and 350 c.c. of ether, and the mixture heated for 4½ hours. After decomposition of the product with ice and ammonium chloride, and remaining over-night, the ethereal layer was separated and the aqueous layer extracted with ether. The ether and the diphenyl were removed, the latter by steam distillation. The residual yellow solid (8 g.) was crystallised from ethyl alcohol until the product, after drying over concentrated sulphuric acid in a vacuum until constant, gave a value which remained unchanged on polarimetric examination after repeated crystallisation.

d-β-*Amino*-ααβ-*triphenylethyl alcohol* is somewhat sparingly soluble in ethyl alcohol and separates in colourless needles, m. p. 129·5—130°, whereas the *r*-isomeride (McKenzie and Barrow, J., 1913, **103**, 1331) melts at 154·5—155°. A trace of it added to concentrated sulphuric acid gives a pink coloration which quickly becomes orange-brown. It is readily soluble in chloroform, ether, benzene or acetone (Found: C = 83·1; H = 6·8. $C_{20}H_{19}ON$ requires C = 83·0; H = 6·6%).

The substance has the opposite sign of rotation to the original ester hydrochloride, being strongly lævorotatory in chloroform: $l = 2$, $c = 1{\cdot}276$, $\alpha_D^{15°} - 6{\cdot}19°$, $[\alpha]_D^{15°} - 243°$. In benzene: $l = 2$, $c = 2{\cdot}027$, $\alpha_D^{17·5°} - 9{\cdot}45°$, $[\alpha]_D^{17·5°} - 233°$.

The *l*-ester hydrochloride (5 g.) was acted on by magnesium

phenyl bromide under conditions similar to those just described. Yield of crude amino-alcohol = 6 g. It was purified by crystallisation from ethyl alcohol.

l-β-*Amino*-ααβ-*triphenylethyl alcohol* has m. p. 129·5—130° (Found : N = 4·9. $C_{20}H_{19}ON$ requires N = 4·8%). The compound is strongly dextrorotatory in chloroform : $l = 2$, $c = 1{\cdot}304$, $\alpha_D^{15.5°} + 6{\cdot}34°$, $[\alpha]_D^{15.5°} + 243°$. $l = 2$, $c = 1{\cdot}304$, $\alpha_{5461}^{15°} + 7{\cdot}63°$, $[\alpha]_{5461}^{15°} + 293°$. In benzene : $l = 2$, $c = 2{\cdot}017$, $\alpha_D^{16°} + 9{\cdot}44°$, $[\alpha]_D^{16°} + 234°$.

Action of Nitrous Acid on d-β-*Amino*-ααβ-*triphenylethyl Alcohol.*—A solution of the *d*-amino-alcohol (0·68 g.) in 50 c.c. of dilute acetic acid was cooled in a freezing mixture of ice and salt, and a solution of 0·5 g. of sodium nitrite in 5 c.c. of water added during 20 minutes. The solid (0·6 g.) which separated was crystallised from ethyl alcohol, and 0·42 g. of phenyldeoxybenzoin, needles, m. p. 134—135°, was obtained. It gave the characteristic emerald-green coloration with concentrated sulphuric acid. Its solution in chloroform was optically inactive.

Isomeric Camphorsulphonates of the d- *and* l-*Amino-Alcohols.*—l-β-*Amino*-ααβ-*triphenylethanol* d-*camphorsulphonate*, prepared by combining the *l*-amino-alcohol (1 mol.) with *d*-camphor-β-sulphonic acid (1 mol.) in ethyl-alcoholic solution, separates in needles, m. p. 200—201° (decomp.) (Found : S = 6·3. $C_{10}H_{16}O_4S$ requires S = 6·1%). In ethyl alcohol : $l = 2$, $c = 0{\cdot}8568$, $\alpha_D^{17°} + 2{\cdot}08°$, $[\alpha]_D^{17°} + 121°$; $l = 2$, $c = 0{\cdot}8568$, $\alpha_{5461}^{15·5°} + 2{\cdot}41°$, $[\alpha]_{5462}^{15·5°} + 143°$.

The enantiomorphously related d-β-*amino*-ααβ-*triphenylethanol* l-*camphorsulphonate* separates from ethyl alcohol in needles, m. p. 200—201° (decomp.) (Found : N = 2·9. $C_{20}H_{19}ON$ requires N = 2·7%). In ethyl alcohol : $l = 2$, $c = 0{\cdot}80$, $\alpha_D^{16°} - 1{\cdot}91°$, $[\alpha]_D^{16°} - 119°$; $l = 2$, $c = 0{\cdot}80$, $\alpha_{5461}^{15°} - 2{\cdot}31°$, $[\alpha]_{5461}^{15°} - 144°$.

l-β-*Amino*-ααβ-*triphenylethanol* l-*camphorsulphonate* separates from ethyl alcohol in needles, m. p. 213·5—214·5° (decomp.). In ethyl alcohol : $l = 2$, $c = 0{\cdot}4448$, $\alpha_D^{16·5°} + 0{\cdot}68°$, $[\alpha]_D^{16·5°} + 76°$; $l = 2$, $c = 0{\cdot}4448$, $\alpha_{5461}^{16°} + 0{\cdot}76°$, $[\alpha]_{5461}^{16°} + 85°$.

The enantiomorphously related d-β-*amino*-ααβ-*triphenylethanol* d-*camphorsulphonate* separates from ethyl alcohol in needles, m. p. 213·5—214·5° (decomp.) (Found : S = 6·2. $C_{10}H_{16}O_4S$ requires S = 6·1%). In ethyl alcohol : $l = 2$, $c = 0{\cdot}40$, $\alpha_D^{16°} - 0{\cdot}61°$, $[\alpha]_D^{16°} - 76°$; $l = 2$, $c = 0{\cdot}40$, $\alpha_{5461}^{15°} - 0{\cdot}72°$, $[\alpha]_{5461}^{15°} - 90°$.

It is insoluble in most organic solvents, moderately soluble in hot ethyl alcohol or water, and sparingly soluble in these solvents at the ordinary temperature. The concentrations employed in the determination of specific rotatory power were necessarily low, so that the values for the specific rotatory power have little significance.

Attempts were made to resolve the *r*-amino-alcohol by *d*-camphor-

β-sulphonic acid both in aqueous and ethyl-alcoholic solution. The progress of the resolution was, however, too slow to enable the method to be used as a preparative one for the *d*- and *l*-amino-alcohols.

Action of Magnesium Phenyl Bromide on α-Aminohydratropic Acid.—The amino-acid (6 g.; 1 mol.), prepared according to McKenzie and Clough (J., 1912, **101**, 390), was added in instalments (½ hour) to the Grignard reagent (12 mols.) prepared from bromobenzene (71 g.), and the mixture was heated for 10½ hours. After decomposition with ice and ammonium chloride, the remaining solid was extracted with ether and the solution added to the main ethereal solution. The ether and diphenyl were removed; the resulting oil solidified. Yield: 5 g. It was triturated with light petroleum, and the solid then crystallised from rectified spirit until pure. Yield: 2 g.

β-Amino-ααβ-triphenyl-β-methylethyl alcohol separates from rectified spirit in rectangular plates, is soluble in benzene and chloroform, and melts at 113—114° (Found: C = 83·0; H = 7·2; N = 4·8. $C_{21}H_{21}ON$ requires C = 83·1; H = 7·0; N = 4·6%). A trace of this compound added to concentrated sulphuric acid produces an orange coloration, which changes quickly to a permanent crimson colour.

Action of Magnesium Phenyl Bromide on r-Phenylalanine.—No visible action took place when *r*-phenylalanine (3 g.; 1 mol.) was gradually added to the Grignard reagent (12 mols.) prepared from 34 g. of bromobenzene. The mixture was heated for 20 hours, and then the additive compound was decomposed with ice and ammonium chloride. The ethereal layer was withdrawn, and then the ether and diphenyl were removed from it in the usual manner. The residual solid amounted to 4 g., which were crystallised from ethyl alcohol. The yield of pure amino-alcohol was 2·4 g., corresponding in crystalline form and melting point with *r*-β-amino-αα-diphenyl-β-benzylethyl alcohol, which was prepared by McKenzie and Richardson (J., 1923, **123**, 79) from the ethyl ester hydrochloride of phenylalanine by the action of magnesium phenyl bromide.

Action of Magnesium Phenyl Bromide on d-Phenylalanine.—*r*-Phenylalanine was resolved by the alkaloidal method of E. Fischer and Schoeller (*Annalen*, 1907, **357**, 2), and *d*-phenylalanine was isolated with a specific rotation in aqueous solution of + 35·0° ($l = 2$, $c = 2·043$, $\alpha_D + 1·43°$), this value being identical with that quoted by Fischer and Schoeller. Three g. of this amino-acid were treated in the manner recorded in the above experiment, with the exception that the mixture was heated for 24 instead of

20 hours. 4·2 G. of crude amino-alcohol were obtained, and were crystallised from ethyl alcohol several times until a steady value for the specific rotation was obtained in chloroform: $l = 2$, $c = 2·0472$, $\alpha_D^{16·5°} + 3·48°$, $[\alpha]_D^{16·5°} + 85·0°$; $l = 2$, $c = 2·0472$, $\alpha_{5461}^{18·5°} + 4·06°$, $[\alpha]_{5461}^{18·5°} + 99·2°$. In benzene: $l = 2$, $c = 2·0512$, $\alpha_D^{19°} + 4·32°$, $[\alpha]_D^{19°} + 105·3°$; $l = 2$, $c = 2·0512$, $\alpha_{5461}^{18°} + 5·03°$, $[\alpha]_{5461}^{18°} + 122·6°$.

This compound has the same sign of rotation as the original amino-acid, and, since no configurative change can take place in the transformation of the amino-acid into the amino-alcohol, it is accordingly designated as d-β-*amino*-αα-*diphenyl*-β-*benzylethyl alcohol*. It crystallises from ethyl alcohol in flat, glassy needles, m. p. 143—144°, is soluble in acetone, benzene, chloroform, ether, or toluene, but is insoluble in water (Found: N = 4·6. $C_{21}H_{21}ON$ requires N = 4·6%). A trace of the compound added to concentrated sulphuric acid produces an orange-brown coloration, which quickly changes to pale pink and then gradually fades. This coloration is also observed with the corresponding *r*-amino-alcohol.

Hydrolysis of Ethyl l-*Phenylaminoacetate Hydrochloride*.—The *l*-ester hydrochloride (1 g.) in 30 c.c. of ethyl-alcoholic potassium hydroxide (0·4487*N*) remained for 24 hours at the ordinary temperature, and was then heated on the water-bath for 30 minutes. The alcohol was removed under diminished pressure, the residue dissolved in water, and the solution extracted with benzene to remove any trace of unchanged ester. The aqueous solution was then neutralised with hydrochloric acid, and the amino-acid (0·5 g.) was separated. Its specific rotation was determined as follows: 0·3719 g. was dissolved in 3·35 c.c. of *N*-hydrochloric acid and 1·5 c.c. of water, $l = 0·5$, $p = 7·193$, $d_4^{20} = 1·0286$, $\alpha_D - 0·46°$, $[\alpha]_D - 12·4°$. The ester hydrochloride was completely hydrolysed.

Partial Deamination of l-*Phenylaminoacetic Acid*.—A solution of sodium nitrite (0·41 g.) in water (2 c.c.) was added drop by drop (30 minutes) to a solution of the *l*-amino-acid (2 g.) in *N*-sulphuric acid (30 c.c.) at 0°. After 5 hours at 0° and 18 hours at the ordinary temperature, the amino-acid (1·35 g.) was precipitated by the addition of ammonia in slight excess. 0·7438 G. was dissolved in 6·7 c.c. of *N*-hydrochloric acid and 3 c.c. of water, $l = 1$, $p = 7·193$, $d_4^{20} = 1·0286$, $\alpha_D - 11·36°$, $[\alpha]_D - 153·5°$, whereas the original *l*-acid had $[\alpha]_D - 156°$ under similar conditions.

The ammoniacal solution, from which the amino-acid had been separated, was acidified with dilute hydrochloric acid, and extracted with ether. The resulting mandelic acid (0·23 g.) was slightly dextrorotatory in aqueous solution: $l = 2$, $c = 1·055$, $\alpha_D + 0·13°$.

Deamination of Ethyl l-*Phenylaminoacetate*.—*Method of E. Fischer and Weichhold*. These authors acted on the *d*-ester with nitrous

acid and obtained a lævorotatory ethyl mandelate with about $[\alpha]_D - 10°$ in acetone solution. On following their directions, using ethyl *l*-phenylaminoacetate (0·90 g.) in place of the *d*-ester, the resulting mandelic ester (0·325 g.) was dextrorotatory. A 10% solution gave $\alpha_D + 0·45°$ in a 0·5 dcm.-tube, so that the value for the specific rotation is approximately $+ 9°$. The result of Fischer and Weichhold was thus confirmed. It should be stated that after the addition of the nitrite, the solution remained over-night at the ordinary temperature. The large amount of racemisation which accompanied this change is apparent when it is recalled that ethyl *l*-mandelate has, according to Walden (*Z. physikal. Chem.*, 1895, **17**, 705), $[\alpha]_D - 90·6°$ in acetone solution.

The dextrorotatory ester obtained above gave a negative result when tested for nitrogen. It was hydrolysed by 4·5 c.c. of aqueous potassium hydroxide (0·5755*N*) at the ordinary temperature for 18 hours. The solution was extracted with ether to remove any unsaponified ester, and the mandelic acid isolated from the aqueous solution as usual. The resulting acid (0·14 g.) was dextrorotatory in aqueous solution: $l = 2$, $c = 0·622$, $\alpha_D + 0·27°$.

Method of Marvel and Noyes. A solution of sodium nitrite (1·6 g.) in water (2·5 c.c.) was added drop by drop with constant stirring for 30 minutes to a solution of ethyl *l*-phenylaminoacetate hydrochloride (5·4 g.) in *N*-sulphuric acid (33 c.c.), the temperature being kept at 0° throughout. A yellow oil separated. After 1 hour at 0° and 2 hours at the ordinary temperature, the solution was extracted with ether, the ethereal solution dried with anhydrous sodium sulphate, and the ether expelled. The resulting oil was distilled, and the portion (1·5 g.) b. p. 127—132°/18 mm. collected. In acetone: $l = 2$, $c = 10$, $\alpha_D - 0·35°$.

The product obtained by Marvel and Noyes was also lævorotatory.

When this oil was tested for nitrogen, it gave a positive result. On hydrolysis under conditions similar to those described in the previous experiment, it gave a mandelic acid (0·8 g.) which was slightly dextrorotatory in aqueous solution: $l = 2$, $c = 3·109$, $\alpha_D + 0·10°$.

This shows that the lævorotation observed by Marvel and Noyes was not due to ethyl *l*-mandelate, but rather to the presence of an intermediate lævorotatory diazo-compound, which gradually passes into ethyl *d*-mandelate with lapse of time. That this view is probable appears from the result of the second experiment quoted below.

The unattacked ethyl phenylaminoacetate hydrochloride was recovered from the aqueous solution remaining after the extraction

of the deamination product with ether. The solution was made alkaline with ammonia, extracted with benzene, the benzene solution dried, and dry hydrogen chloride passed in to precipitate the ester hydrochloride. The latter was filtered off. Yield: 2 g. In aqueous solution: $l = 1$, $c = 5{\cdot}07$, $\alpha_D - 4{\cdot}59°$, $[\alpha]_D - 90{\cdot}5°$. The regenerated hydrochloride had thus practically the same rotation as the original.

In a second experiment where 7 g. of the *l*-ester hydrochloride were employed, the conditions of deamination were exactly similar to those just described except that the solution after being kept at 0° was allowed to remain for 3½ instead of 2 hours. The resulting oil (2 g.), which gave a positive test for nitrogen, was in this case dextrorotatory in acetone solution: $l = 1$, $c = 10$, $\alpha_D + 0{\cdot}30°$.

On hydrolysis with aqueous alkali under similar conditions to those adopted in the other experiments, the resulting mandelic acid was dextrorotatory in aqueous solution: $l = 2$, $c = 3{\cdot}32$, $\alpha_D + 0{\cdot}19°$.

The amino-ester hydrochloride was recovered as before. In aqueous solution: $l = 1$, $c = 5{\cdot}07$, $\alpha_D - 4{\cdot}57°$, $[\alpha]_D - 90{\cdot}1°$.

We desire to express our best thanks to the Department of Scientific and Industrial Research and to the Carnegie Trust for their assistance. We are also indebted to Dr. H. J. Plenderleith for his assistance in the deamination of β-amino-αα-diphenyl-*n*-propyl alcohol.

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UNIVERSITY OF ST. ANDREWS. [*Received, December 5th*, 1924.]

XLVII.—*The Action of Caustic Alkali on α-Bromo-α-ethylbutyrylcarbamide.*

By GEORGE NEWBERY.

THE action of water, caustic alkali and of pyridine on α-bromo-α-ethylbutyrylcarbamide (adalin), $CBrEt_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, was investigated by Rosenmund and Hermann (*Ber. deut. pharm. Ges.*, 1912, **22**, 96), who considered the main product, m. p. 185°, to be 5 : 5-diethylhydantoin. This substance, prepared according to those authors, melted when pure at 198° and was, moreover, identical with a product invariably obtained in experiments involving the condensation of adalin in alkaline solution and also from the condensation, if not adequately controlled, of α-bromo-α-ethylbutyryl bromide and carbamide. 5 : 5-Diethylhydantoin

(Errara, *Gazzetta*, 1896, **26**, i, 207; Ingold, Sako, and Thorpe, J., 1922, **121**, 1193) has m. p. 165° and is readily converted by dilute alkali into a salt of diethylhydantoic acid; under the same conditions the substance, m. p. 198°, remains unchanged.

After the reaction between 2*N*-sodium hydroxide (rather more than 1 mol.) and α-bromo-α-ethylbutyrylcarbamide, three main products were isolated: the substance, m. p. 198°; an unsaturated acid oil, b. p. 200—210°/760 mm., which was shown to be a mixture of the isomeric forms of α-ethylcrotonic acid; and a saturated acid, b. p. 283—286°/760 mm., which corresponded in properties with the oil to which Rosenmund and Hermann ascribed the formula $C_{13}H_{20}O_6N_2$. No evidence of the formation of diethylhydantoin nor of the unsaturated substance, m. p. 91°, described by these authors as α-ethylcrotonylcarbamide, could be obtained.

Analysis of the substance m. p. 198° gave figures in satisfactory agreement with the formula $C_7H_{12}O_2N_2$ and, although it did not readily decolorise solutions of bromine (whilst in common with adalin it is readily oxidised by alkaline permanganate), its behaviour on hydrolysis showed clearly that it must be regarded as a ureide of α-ethylcrotonic acid (I). Hydrolysis by alcoholic potash led to the formation of an unsaturated neutral substance, m. p. 118°, and to a mixture of the two α-ethylcrotonic acids. Analysis and further hydrolysis by prolonged boiling with 20% caustic soda solution indicated that the neutral substance was an amide of α-ethylcrotonic acid (II). That this was actually the case was proved by its synthesis from α-ethylcrotonyl chloride and ammonia.

The action of α-ethylcrotonyl chloride on carbamide, or of phosphoryl chloride on a mixture of either of the forms of α-ethylcrotonic acid and carbamide, yielded an isomeric unsaturated ureide, m. p. 158°, which showed no readiness to decolorise bromine solutions and on hydrolysis gave the unsaturated amide, m. p. 118°, together with the solid form of α-ethylcrotonic acid. The ureides, m. p. 198° and 158° respectively, are therefore probably geometrical isomerides of the unsaturated ureide (I).

Small amounts of the lower-melting isomeride and of an isomeric α-ethylcrotonamide, m. p. 104°, were also isolated from the treatment of α-bromo-α-ethylbutyrylcarbamide with alkali. This amide was also obtained, in better yield, by the action of excess (2 mols.) of caustic alkali and was remarkably stable when heated with moderately strong alkali, but on prolonged hydrolysis with very concentrated aqueous caustic soda it gave only ammonia and a mixture of the isomeric α-ethylcrotonic acids. It is identical with the amide, m. p. 99°, obtained by Mannich and Zernik (*Arch. Pharm.*, 1908, **246**, 183) by the action of water on α-bromo-α-ethyl-

butyramide (neuronal); a preparation thus made also melted at 104° (corr.).*

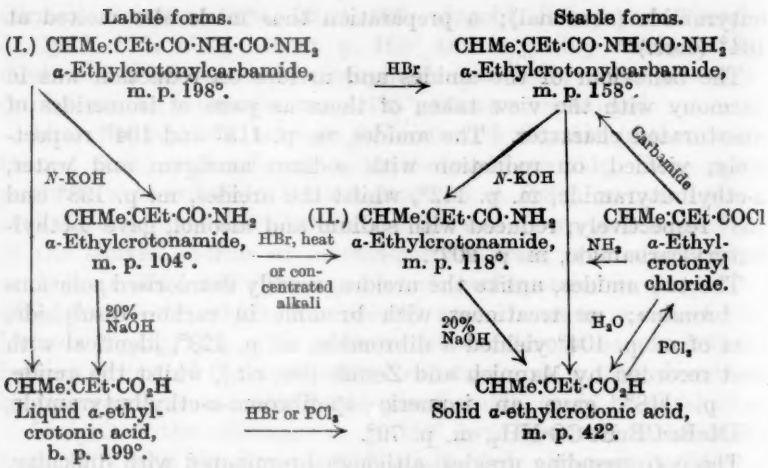
The behaviour of the amides and ureides on reduction was in harmony with the view taken of them as pairs of isomerides of unsaturated character. The amides, m. p. 118° and 104° respectively, yielded, on reduction with sodium amalgam and water, α-ethylbutyramide, m. p. 112°, whilst the ureides, m. p. 198° and 158° respectively, reduced with sodium and alcohol, gave α-ethylbutyrylcarbamide, m. p. 207°.

The two amides, unlike the ureides, readily decolorised solutions of bromine; on treatment with bromine in carbon disulphide, that of m. p. 104° yielded a dibromide, m. p. 128°, identical with that recorded by Mannich and Zernik (*loc. cit.*), whilst the amide, m. p. 118°, gave an isomeric αβ-dibromo-α-ethylbutyramide, $CHMeBr{\cdot}CBrEt{\cdot}CO{\cdot}NH_2$, m. p. 79°.

The corresponding ureides, although brominated with difficulty, yielded under suitable conditions dibromides, m. p. 143° and 112° respectively, presumably racemic forms of αβ-dibromo-α-ethylbutyrylcarbamide, $CHMeBr{\cdot}CBrEt{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$. Although the unsaturated amides react additively with bromine far more readily than the corresponding ureides, the addition of the elements of hydrogen bromide to the former has so far not been achieved. The transformation of the more fusible to the less fusible amide is, however, brought about by treatment with hydrobromic acid, as it is also by concentrated alkali or by heat. On the other hand, the higher-melting ureide is apparently the labile form, since it is converted into that of lower melting point by boiling with hydrobromic acid. From either isomeride a small yield of β-bromo-α-ethylbutyrylcarbamide, $CHMeBr{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 179°, is obtained by the action of the same reagent. The product is of some interest as an isomeride of adalin.

The relationships of the ureides and amides to one another and to the isomeric α-ethylcrotonic acids are tabulated on p. 298. The stable forms of ureide, amide, and acid, alone are obtained from the acid chloride (compare Blaise and Bagard, *Ann. Chim.*, 1907, [viii], **11**, 129) and the labile forms of ureide and amide, on hydrolysis with concentrated alkali, yield the liquid form of α-ethylcrotonic acid slightly contaminated with the stable form, whereas the isomerides yield the stable form alone.

* Recently, Auwers (*Annalen*, 1923, **432**, 77) has described the preparation of an amide of α-ethylcrotonic acid, m. p. 114—115°, from α-ethylcrotonyl chloride and ammonia in ethereal solution. He was, however, apparently unable to isolate the lower-melting amide by the method of Mannich and Zernik, the amide, m. p. 114—115°, being alone obtained.



The acid oil, b. p. 283—286°, to which Rosenmund and Hermann ascribed the formula $C_{13}H_{20}O_6N_2$, solidified on standing in the ice-chest and then had m. p. 24°. Analysis gave no figures in satisfactory agreement with a simple formula, but the substance, which behaved as a dibasic acid, gave, on hydrolysis, diethylglycollamide, $OH{\cdot}CEt_2{\cdot}CO{\cdot}NH_2$, m. p. 88°, and diethylglycollic acid, $OH{\cdot}CEt_2{\cdot}CO_2H$, m. p. 79—80°, and was thus recognised as the symmetrical bisdiethylglycollylcarbamide, $(OH{\cdot}CEt_2{\cdot}CO{\cdot}NH)_2CO$, described by Clemmensen and Heitman (*Amer. Chem. J.*, 1908, **40**, 287); when purified essentially by their method, it had m. p. 29° and corresponded with the formula $C_{13}H_{24}O_5N_2$. Its silver salt reacted with ethyl iodide to produce *bis-α-ethoxy-α-ethylbutyrylcarbamide*, $(OEt{\cdot}CEt_2{\cdot}CO{\cdot}NH)_2CO$, b. p. 240°, which gave, on hydrolysis, *α-ethoxy-α-ethylbutyramide*, m. p. 36°.

The presence of alkali cyanide in the reaction mixture from the action of caustic alkali on α-bromo-α-ethylbutyrylcarbamide, noted by Rosenmund and Hermann and confirmed by the present author, is probably to be accounted for by the intermediate formation of a small amount of α-bromo-α-ethylbutyramide. The latter was shown by Mannich and Zernik (*loc. cit.*) to give, on treatment with caustic soda, diethyl ketone and hydrobromic and hydrocyanic acids (compare also Mossler, *Monatsh.*, 1908, **29**, 69). The amount of diethyl ketone isolated, as semicarbazone from the main reaction mixture, was in approximate agreement with that required by the assumption that sodium cyanide had been formed in equimolecular quantity.

Treatment of α-bromo-α-ethylbutyrylcarbamide and the α-ethylcrotonylcarbamides with *N*- or 2*N*-alkali always led to the pro-

duction of larger quantities of the mixed α-ethylcrotonic acids than would be expected on the assumption that the corresponding amides are necessarily intermediate products of the hydrolysis. It seems probable, therefore, since under similar conditions of time, concentration of alkali, etc., the unsaturated amides are not appreciably hydrolysed to the corresponding acids, that the hydrolysis of the unsaturated ureides proceeds in two directions :—

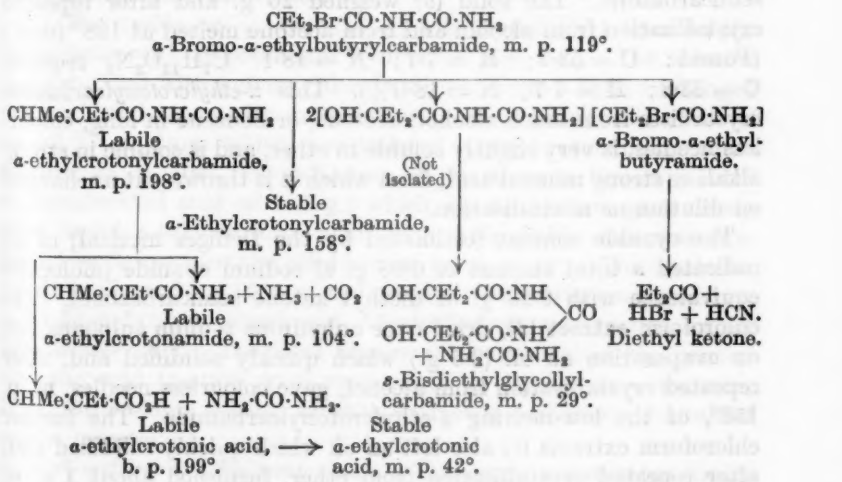
(*a*) $CHMe{:}CEt{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + H_2O \longrightarrow CHMe{:}CEt{\cdot}CO_2H + NH_2{\cdot}CO{\cdot}NH_2$.

(*b*) $CHMe{:}CEt{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + H_2O \longrightarrow CHMe{:}CEt{\cdot}CO{\cdot}NH_2 + NH_3 + CO_2$.

Under certain conditions, the carbamide formed in the action (*a*) escapes complete hydrolysis to ammonia and carbon dioxide and can be isolated in part as the characteristic nitrate.

Bisdiethylglycollylcarbamide, on the other hand, was hydrolysed by mild treatment with alkali to the stable amide, and only further to diethylglycollic acid under the more drastic conditions necessary to hydrolyse the amide.

Finally, the small amount of the stable form of α-ethylcrotonylcarbamide isolated from the action of 2*N*-caustic soda solution on adalin appears to be derived directly from the latter by the elimination of hydrogen bromide, and not by the isomerisation of its labile isomeride, since no conversion of the latter on treatment with alkali of this concentration could be detected.



EXPERIMENTAL.

Action of Sodium Hydroxide (1 *mol.*) *on α-Bromo-α-ethylbutyrylcarbamide.*—Commercial adalin of m. p. 119° (100 g.) was treated

with gently boiling 2*N*-sodium hydroxide (270 c.c.; rather more than 1 equiv.) in an apparatus through which a current of air could be aspirated and passed in sequence through sufficient of a hot 2*N*-solution of sulphuric acid to absorb the evolved ammonia, a strong solution of semicarbazide hydrochloride saturated with sodium acetate, and, finally, a little dilute permanganate solution acidified with sulphuric acid. A semicarbazone (*a*) shortly began to separate and as long as there was sufficient excess of semicarbazide there was no appreciable decoloration of the permanganate. After being heated for an hour, the mixture was cooled, the crystalline solid (*b*) filtered off, and the filtrate made up to 500 c.c. Fifty c.c. (*c*) were removed for the titration of cyanide and the remainder was extracted once with chloroform (*d*). The liquors were then saturated with sodium chloride, exhaustively extracted with chloroform (*e*), and acidified (congo-red) with concentrated hydrochloric acid, there being considerable disengagement of carbon dioxide and the liberation of an oily layer, which was completely extracted with ether (*f*) Finally, the mixture was neutralised exactly with caustic soda (phenolphthalein), evaporated to dryness, and the residual salt extracted in a Soxhlet apparatus successively with alcohol and acetone (*g*).

The semicarbazone (*a*), after being washed with a little water, dried (0·2 g.; m. p. 135—136°), and recrystallised from acetone, melted at 139°, alone or mixed with synthetic diethyl ketone semicarbazone. The solid (*b*) weighed 20 g. and after repeated crystallisation from alcohol and from acetone melted at 198° (corr.) (Found: C = 53·7; H = 7·7; N = 18·1. $C_7H_{12}O_2N_2$ requires C = 53·8; H = 7·7; N = 18·0%). This *α-ethylcrotonylcarbamide* crystallises from much alcohol, acetone, or benzene in long, colourless needles, is very slightly soluble in ether, and is soluble in strong alkali or strong mineral acid, from which it is thrown out unchanged on dilution or neutralisation.

The cyanide content (estimated by the Denigès method) of (*c*) indicated a total amount of 0·08 g. of sodium cyanide (molecular equivalence with 0·23 g. of diethyl ketone semicarbazone). The chloroform extract (*d*), dried over anhydrous sodium sulphate, left on evaporation an oil (2·5 g.) which quickly solidified and, after repeated crystallisation from alcohol, gave colourless needles, m. p. 158°, of the low-melting α-ethylcrotonylcarbamide. The further chloroform extracts (*e*) also left an oil which quickly solidified and, after repeated crystallisation from ether, furnished about 1 g. of α-ethylcrotonamide, m. p. 104°. The ethereal extract (*f*), dried over calcium chloride, yielded an oil which on fractionation gave (i) an unsaturated acid oil, b. p. 200—220° (4·7 g.), and (ii) a

saturated acid fraction, b. p. 282—284° (28·2 g.). The former was identified as a mixture of the two forms of α-ethylcrotonic acid and was converted by a drop of concentrated hydrobromic acid or by the successive action of phosphorus trichloride and water into the solid form of the acid, m. p. 42°, not depressed by admixture with a genuine specimen. The examination of the fraction (ii) is described below. The combined extracts (*g*) yielded on evaporation no appreciable residue. The yields of the various products together accounted for practically the whole of the adalin employed.

Hydrolysis of High-melting α-Ethylcrotonylcarbamide.—(*a*) The ureide, m. p. 198° (40 g.) and potassium hydroxide (40 g., dissolved in the minimum of water and diluted with alcohol, 200 c.c.) were heated under reflux for 24 hours. After removal of the excess of alcohol in a vacuum, two layers formed; the upper quickly crystallised and yielded, on being drained, 2·7 g. of crude amide. The liquors yielded to ether 8·5 g. of yellow oil, which gave a further crop of crude amide somewhat contaminated with the lower-melting isomeride. The aqueous liquors, on acidification and ether extraction, gave an unsaturated acid oil (15·5 g.) which, on distillation, gave a fraction, b. p. 195—205° (6·4 g.), and a fraction, b. p. 205—220° (5·0 g.). Both showed marked unsaturation, but neither solidified on cooling. Both, however, yielded α-ethylcrotonic acid, m. p. 42°, on treatment with phosphorus trichloride and subsequently with water.

(*b*) The ureide, m. p. 198° (17 g.) was heated for 1 hour on the water-bath with *N*-potassium hydroxide (350 c.c.). The solution was saturated with sodium chloride, filtered from a little unchanged material, and repeatedly extracted with chloroform; this removed an oil (7 g.) from which was isolated α-ethylcrotonamide, white needles, m. p. 104°. Acidification of the aqueous liquors yielded an unsaturated acid oil (4·3 g.) which, on distillation, gave nearly pure liquid α-ethylcrotonic acid, b. p. 190—200°; this was converted as before into the solid isomeride, m. p. 42°. The combined yields accounted for 95% of the unsaturated ureide employed.

(*c*) In a further experiment, the hydrolysis was carried on for 30 minutes only. The final liquors after removal of the neutral and the acid fraction were evaporated to dryness in a vacuum; from the residue boiling alcohol extracted carbamide (identified as the nitrate).

High-melting α-Ethylcrotonamide.—The crude unsaturated amide from the above preparation (*a*), on repeated crystallisation from ether, formed colourless needles or leaflets, m. p. 118° (corr.) (Found: C = 63·8; H = 10·0; N = 12·4. $C_6H_{11}ON$ requires

C = 63·7; H = 9·7; N = 12·4%). It is very soluble in alcohol, moderately soluble in benzene or water, slightly soluble in cold ether, and insoluble in light petroleum. Prepared synthetically from α-ethylcrotonyl chloride and strong aqueous ammonia, the same amide was obtained in 75% yield in glistening plates, m. p. 118° (Found: N = 12·5%).

Hydrolysis of High-melting α-Ethylcrotonamide.—The unsaturated amide (6·5 g.) was refluxed for 3 hours with 20% aqueous caustic soda (15 c.c.). Ammonia was evolved and, after the extraction of some 3 g. of unchanged amide by chloroform, acidification and ether extraction yielded an acid oil (3 g.), from which α-ethylcrotonic acid was obtained; m. p. 40°.

Action of Sodium Hydroxide (2 mols.) on α-Bromo-α-ethylbutyrylcarbamide.—Finely-powdered commercial adalin (100 g.) was heated under reflux with *N*-sodium hydroxide (1000 c.c.) for 90 minutes and, when cold, the liquid was saturated with sodium chloride, filtered from high-melting α-ethylcrotonylcarbamide (4 g.), and extracted with ether. From the extract, dried over anhydrous sodium sulphate, were obtained 4 g. of a substance which readily sublimed at about 100°, quickly solidified on cooling, and after repeated crystallisation from ether, melted at 104°, alone or mixed with α-ethylcrotonamide (m. p. 104° after several crystallisations), prepared according to Mannich and Zernik (*loc. cit.*).

Low-melting α-ethylcrotonamide crystallises in colourless needles from ether, in which it is more soluble than the high-melting isomeride, is very soluble in alcohol or chloroform, moderately soluble in benzene or water, and insoluble in light petroleum (Found: C = 63·6; H = 9·9; N = 12·5. Calc. for $C_6H_{11}ON$, C = 63·7; H = 9·7; N = 12·4%).

On acidification, the reaction product also yielded a mixture of the two α-ethylcrotonic acids, b. p. 190—220° (11 g.), and the saturated acid oil, b. p. 284—287° (26 g.).

Hydrolysis of Low-melting α-Ethylcrotonamide.—(*a*) α-Ethylcrotonamide, m. p. 104° (6 g.) was heated on the steam-bath for 1 hour with *N*-caustic potash (125 c.c.). Saturation with sodium chloride and chloroform extraction yielded the unchanged amide (5·8 g.; 97% recovery). There was no appreciable acid fraction.

(*b*) The amide (4 g.), boiled under reflux with 20% caustic soda (10 c.c.) for 3 hours, yielded, as before, 3 g. of unsaturated amide m. p. 100° (indefinite), which was probably a mixture of the two isomeric amides, since repeated crystallisation from ether yielded the less soluble form, m. p. 118°. The acid fraction yielded liquid α-ethylcrotonic acid (0·7 g.), b. p. 200°.

(*c*) The amide (3·5 g.), heated for 5 hours with boiling 40%

caustic soda (20 c.c.), yielded, when worked up in a similar way, the high-melting form of the amide (0·25 g.), together with a mixture of the two α-ethylcrotonic acids, b. p. 195—205° (3 g.).

Synthesis of Low-melting α-Ethylcrotonylcarbamide.—α-Bromo-α-ethylbutyryl bromide (200 g.; b. p. 128°/30 mm.) was run slowly into a boiling solution of potassium hydroxide (400 g.) in water (250 c.c.) and alcohol (750 c.c.). Much heat was developed and the alcohol kept boiling vigorously. The mixture was heated for 30 minutes on the steam-bath, water added to dissolve the separated potassium bromide, and the excess of alcohol removed in a vacuum. Acidification with hydrochloric acid and ether extraction yielded a mixture of the two forms of α-ethylcrotonic acid (75 g.; b. p. 190—210; yield 90% of theory). (*a*) To the mixed acids (5 g.) was added phosphoryl chloride (3 g.), followed almost immediately by 8 g. of carbamide. A vigorous reaction ensued which was not controlled and, after 30 minutes' heating on the water-bath, addition of water, and a short period of further heating, the mixture was cooled and the crude carbamide (3·5 g.) filtered off. (*b*) α-Ethylcrotonyl chloride (2·2 g.; b. p. 58°/14 mm.), prepared from the mixed acids and phosphorus trichloride, was heated on the water-bath for 2 hours with carbamide (2·5 g.). The semi-liquid mass became more viscous and was finally nearly solid. Water was added and the crude carbamide (2 g.) filtered off.

Low-melting α-Ethylcrotonylcarbamide, m. p. 158° (corr.) crystallised in colourless needles from alcohol; it was not readily soluble in cold alcohol, benzene, acetone, or ether, and did not readily decolorise bromine water (Found: C = 53·6; H = 7·8; N = 18·1. $C_7H_{12}O_2N_2$ requires C = 53·8; H = 7·7; N = 18·0%).

Hydrolysis of Low-melting α-Ethylcrotonylcarbamide.—The hydrolysis of the ureide, m. p. 158° (5 g.) was effected with *N*-caustic potash (100 c.c.) under exactly similar conditions to those employed for the hydrolysis of the isomeric ureide, m. p. 198°. The chloroform extract yielded an oil (2 g.) which quickly solidified and crystallised from ether in leaflets, m. p. 118°, alone or mixed with synthetic α-ethylcrotonamide. The aqueous liquors after acidification yielded to ether an oil (1·8 g.) which quickly solidified and proved to be solid α-ethylcrotonic acid, m. p. 42°. Hydrolysis for 3 hours with concentrated alcoholic potash yielded the same products.

Reduction of the Isomeric α-Ethylcrotonamides.—A warm solution of α-ethylcrotonamide, m. p. 118° (1 g.) in water (50 c.c.), was reduced with 4% sodium amalgam (50 g.), and, after filtration from mercury, was extracted with chloroform. Desiccation and evaporation of the solvent yielded an oil which solidified on stand-

ing. Repeated crystallisation from ether yielded white needles, m. p. 111°, which did not reduce alkaline permanganate or decolorise bromine water. α-Ethylcrotonamide, m. p. 104°, under the same conditions, yielded the same product.

α-Ethylbutyramide.—α-Ethylbutyryl chloride, b. p. 65°/70 mm. (5 g.), was run slowly with continuous stirring into excess (10 c.c.) of concentrated ammonia solution cooled by ice. The solid which separated, together with a further quantity obtained by chloroform extraction (3·5 g. in all; 82% of theory), crystallised from ether in colourless needles, m. p. 112° (corr.), alone or mixed with the reduction product from either α-ethylcrotonamide (Found: N = 12·3. Calc. for $C_6H_{13}ON$, N = 12·2%). The alkaline hydrolysis of synthetic α-ethylbutyrylcarbamide likewise led to the same saturated amide, m. p. 112° (E. Fischer and Dilthey, *Ber.*, 1902, **35**, 853, give m. p. 107°).

Reduction of the Isomeric α-Ethylcrotonylcarbamides.—Either isomeride (1 g.) was reduced with boiling ethyl alcohol (20 c.c.) and sodium (1·5 g.). Chloroform (50 c.c.) was added to the mixture, followed by water (100 c.c.). The solid (0·4 g.) isolated from the chloroform extract crystallised from alcohol in colourless needles, m. p. 205—206°, which did not reduce a cold alkaline permanganate solution nor depress the m. p. (206—207°) of synthetic α-ethylbutyrylcarbamide.

Bromination of Low-melting α-Ethylcrotonamide.—α-Ethylcrotonamide, m. p. 104° (2·5 g.), suspended in carbon disulphide (30—40 c.c.) at 0°, required the theoretical quantity of bromine in the same solvent to give a permanent coloration after an hour. The crystals, which began to separate during the addition, were washed with carbon disulphide, dried (3·5 g.; 58% of theory), and recrystallised from alcohol, high-melting αβ-dibromo-α-ethylbutyramide separating in colourless needles, m. p. 127—128°, slightly soluble in cold carbon disulphide, ether or petroleum (Found: Br = 58·6. Calc. for $C_6H_{11}ONBr_2$, Br = 58·6%).

Bromination of High-melting α-Ethylcrotonamide.—α-Ethylcrotonamide, m. p. 118° (2·5 g.), treated in a similar way, gave a less sharp end-point, absorption of bromine being less rapid and only towards the end of the addition was there any separation of the dibromide. The solvent was evaporated, the residue, which solidified after some hours at 0°, was washed with ether–petroleum (b. p. 40—60°), and crystallised from the same mixture, yielding low-melting αβ-dibromo-α-ethylbutyramide (2·5 g.; 42% of theory) as a slightly yellow, crystalline powder, m. p. 77—78°; by repeated crystallisation, colourless plates, m. p. 79—80°, were obtained. This dibromide was more soluble in carbon disulphide, alcohol, or

ether than the high-melting isomeride, and was somewhat soluble in hot petroleum (b. p. 40—60°) (Found: Br = 58·5. $C_6H_{11}ONBr_2$ requires Br = 58·6%).

Bromination of Low-melting α-Ethylcrotonylcarbamide.—α-Ethylcrotonylcarbamide, m. p. 158° (5 g.) was exposed for 48 hours over excess of bromine in a closed desiccator. Excess of bromine was removed in a current of air, and the residue refluxed with ether (200 c.c.). After filtration, the ethereal solution was concentrated to 20 c.c., and the crystals (3 g.) which separated were recrystallised from alcohol, when low-melting *αβ-dibromo-α-ethylbutyrylcarbamide* was obtained in colourless needles, m. p. 112° (Found: Br = 50·7. $C_7H_{12}O_2N_2Br_2$ requires Br = 50·6%).

Bromination of High-melting α-Ethylcrotonylcarbamide.—The ureide, m. p. 198° (5 g.), brominated in a similar manner, gave high-melting *αβ-dibromo-α-ethylbutyrylcarbamide* (3·2 g.), which crystallised from alcohol in colourless prisms, m. p. 142—143°. It is moderately soluble in ether (Found: Br = 50·4. $C_7H_{12}O_2N_2Br_2$ requires Br = 50·6 %).

Action of Hydrogen Bromide on Low-melting α-Ethylcrotonamide.—α-Ethylcrotonamide, m. p. 104° (2·5 g.) was heated on the water-bath for 2 hours with acetic acid saturated with hydrogen bromide at 0° (25 c.c.). Excess of the acids was removed in a vacuum, the residue (10 c.c.) nearly neutralised with 2*N*-sodium hydroxide, and the mixture extracted with chloroform. The solid (0·6 g.) which remained after the removal of the solvent, crystallised from ether in leaflets, m. p. 117—118°, not depressed by admixture with the synthetic amide, m. p. 118°.

Behaviour of Hydrogen Bromide with High-melting α-Ethylcrotonamide.—The amide, m. p. 118° (0·3 g.) was heated for 6 hours in a sealed tube at 100° with acetic acid saturated with hydrogen bromide at 0° (2 c.c.). The mixture, after dilution and neutralisation, gave, on extraction, only the unchanged amide, m. p. 118°.

Action of Hydrogen Bromide on Low-melting α-Ethylcrotonylcarbamide.—A mixture of the ureide, m. p. 158° (4 g.), with acetic acid saturated with hydrogen bromide at 0° (40 c.c.) was heated under reflux for 20 hours on the steam-bath and when poured into cold water (500 c.c.) yielded a solid product (1 g.).

β-Bromo-α-ethylbutyrylcarbamide was obtained in colourless needles, m. p. 179—180°, by repeated crystallisation from alcohol. It is sparingly soluble in alcohol, benzene, or ether (Found: N = 11·9; Br = 33·4. $C_7H_{13}O_2N_2Br$ requires N = 11·8; Br = 33·75%).

Action of Hydrogen Bromide on Low-melting α-Ethylcrotonylcarbamide.—The ureide, m. p. 198° (5 g.) together with saturated acetic-hydrobromic acid (30 c.c.) was heated for 8 hours in a sealed

bottle in a boiling-water bath. The mixture was filtered from a little ammonium bromide, water added, and the solution nearly neutralised with 20% caustic soda solution. On cooling, a white solid (4 g.) separated, which, after repeated crystallisation from alcohol, melted at 177° and was identical with the β-bromo-α-ethylbutyrylcarbamide described above. Chloroform extraction of the still slightly acid mother-liquors yielded a small amount of oil, which solidified on standing and after repeated crystallisation from alcohol had m. p. 158°, not depressed by admixture with the unsaturated ureide of that melting point.

Examination of the Saturated Acid, b. p. 283—286°.—Bisdiethylglycollylcarbamide was obtained in a pure condition from the acid oil, b. p. 283—286°, by a slight modification of the method proposed by Clemmensen and Heitman (*loc. cit.*) involving the preparation of the silver salt from the ammonium salt, followed by the decomposition of the former by hydrogen sulphide. It then melted at 29° and agreed in physical and chemical properties with those of bisdiethylglycollylcarbamide prepared synthetically (Found: C = 54·1, 54·0; H = 8·1, 8·3; N = 9·8, 9·7. Calc. for $C_{13}H_{24}O_5N_2$, C = 54·1; H = 8·3; N = 9·7%).

Hydrolysis of Bisdiethylglycollylcarbamide.—(*a*) The oil, b. p. 283—286° (21 g.) was refluxed for 48 hours on the steam-bath with alcoholic potash from potassium hydroxide (21 g.) dissolved in the minimum of water and 100 c.c. of alcohol. Ammonia was evolved during the whole period of heating. The mixture yielded on dilution and ether extraction an oil, b. p. 164°/25 mm. (10 g.). This quickly solidified and on crystallisation from ether gave diethylglycollamide, m. p. 88°, in colourless, hexagonal plates (Found: N = 10·8. $C_6H_{13}O_2N$ requires N = 10·7%). The aqueous liquors on acidification likewise yielded an acid fraction (10 g.) which, on distillation, boiled for the most part at 115—130°/10 mm. There was a small amount of unchanged material b. p. 152—155°/10 mm. The main fraction quickly solidified and crystallised from petroleum (b. p. 60—80°) in colourless needles, m. p. 80°, not depressed by admixture with synthetic diethylglycollic acid, m. p. 81°. (*b*) The same oil (40 g.), hydrolysed under the same conditions for 3 hours only, yielded diethylglycollamide (15 g.) and unchanged material (10 g.). No diethylglycollic acid could be isolated. (*c*) The oil (13 g.), boiled on the sand-bath for 1 hour with 2*N*-caustic soda, gave no diethylglycollamide, and the acid fraction yielded only unchanged material (12·5 g.).

Bis-α-ethoxy-α-ethylbutyrylcarbamide.—The silver salt (19 g.) of bisdiethylglycollylcarbamide (Found: Ag=40·1. $C_{13}H_{22}O_5N_2Ag_2,2H_2O$ requires Ag = 40·1%) from the saturated acid oil, b. p. 283—286°,

after being dried at 100°, was heated with ethyl iodide (25 c.c.) for 15 minutes, silver iodide was removed by filtration, and the oil (12 g.; 97% of theory), which was insoluble in caustic soda, distilled at 160—170°/60 mm. The oil so obtained had a characteristic odour of garlic and b. p. 240° (Found: C = 59·0; H = 9·3. $C_{17}H_{32}O_5N_2$ requires C = 59·3; H = 9·3%). A preparation in a similar way from synthetic bisdiethylglycollylcarbamide yielded the same product.

Hydrolysis of Bis-α-ethoxy-α-ethylbutyrylcarbamide.—The ethoxycarbamide (20 g.) was hydrolysed for 12 hours on the steam-bath with alcoholic potash from potassium hydroxide (20 g.) in the minimum of water and 200 c.c. of alcohol. After the removal of excess alcohol in a vacuum and dilution, ether extraction gave an oil (10 g.), b. p. 141—144°/11 mm., which solidified after remaining a few hours at 0°.

α-Ethoxy-α-ethylbutyramide, when pure, melts at 36° and is very soluble in most organic solvents, but practically insoluble in light petroleum. It could not be crystallised satisfactorily and was apparently best purified by repeated distillation in a vacuum (Found: N = 8·7. $C_8H_{17}O_2N$ requires N = 8·8%). The aqueous liquors from this preparation yielded practically no acid fraction, and ethoxyethylbutyramide was found to be extremely resistant to the hydrolytic action of alkali.

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